



## SYSTEM

OF

CHEMISTRY.

#### IN FIVE VOLUMES.

By THOMAS THOMSON,

M.D. F.R.S.E.

THE FOURTH EDITION.

VOL. II.

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1810.

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## SYSTEM Compound bodies are of two kinds. Some of them

are formed by the combination of two or more simple anheisunes with each other. Thus phosphorie acid is

compounds. All these of amstances render the com-

#### CHEMISTRY. combi nation of two or more compound bodies with each other,

Thus, phosphöre of a manual is compared of phosphoric acid and annotants ; volatile instment, anothind ammo-

#### nis. The first of these kinds of compounds I call Par-BOOK II. SECONDARY COMPOUNDS. If will be very convenient

#### OF COMPOUND BODIES. Boldes the 15 bothes described in the mereding

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COMPOUND BODIES are substances composed of two or more simple bodies combined together. Now as the simple bodies described in the preceding book, excluding light and heat, are 35 in number, if they were all capable of combining together, the compounds formed by them would amount to a great many thousands: But all the simple substances are not capable of combining with each other; azote, for instance, has never been combined with metals. This diminishes their number considerably. Besides, we are still too little acquainted with the nature of caloric and light to be able to treat separately of the compounds into which they enter. Several numerous classes of compounds have been already described in the last Book; for the oxides, sulphurets, phosphurets, and alloys, are real Vol. II.

Book II.

2 408

Book If.

compounds. All these circumstances render the compounds which form the subject of this Book much less numerous than might be at first supposed.

Divisions.

Compound bodies are of two kinds. Some of them are formed by the combination of two or more simple substances with each other. Thus phosphoric acid is composed of phosphorus and oxygen; and oil, of hydrogen and carbon. Others are formed by the combination of two or more compound bodies with each other. Thus phosphate of ammonia is composed of phosphoric acid aud ammonia; volatile liniment, of oil and ammonia. The first of these kinds of compounds I call PRI-MARY COMPOUNDS; to the second I give the name of SECONDARY COMPOUNDS. It will be very convenient to describe each of them separately.

Salifiable bases.

Besides the 35 bodies described in the preceding Book, there are a number of others lately discovered by the sagacity of Professor Davy, and which we omitted for reasons formerly specified. These, when combined with oxygen, constitute the important classess of bodies known under the names of alkalies and earths. These substances form a distinct order by themselves, and which, for that reason, may be described separately. Now these bodies (including the volatile alkali) have the property of combining with acids, and of constituting the bases of a very numerou set of bodies called salts. This induced Lavoisier to give them the appellation of salifiable bases : a name which I shall adopt, though it be somewhat exceptionable, because I can think of no other which is not equally so. This Book then shall be divided into three parts : I. SALIFIABLE BASES. II. PRIMARY COMPOUNDS. 111. SECONDARY COMPOUNDS. Intering any on fire , abit Fal. 11.

#### SALIFIABLE BASES.

Chap. 1

DIVISION I.

SALIFIABLE BASES.

The word susarity to a Arabita or gin, and was introduced into chemistry after it and been applied to a

ASTINIA DELTAJOJ

In the class of salifiable bases, it is proper to include ammonia, because its properties connect it with the most important of the other substances. The salifiable bases naturally arrange themselves under the four following heads:

- benfutdo od yan iladia v ... ezonatici lo epote od Po 1. Volatile alkalies
- . Fixed alkalies. od tadi borovosih
- 3. Alkaline earths.
- and some part of the definition of the second states of the second state

These shall form the subject of the four following Chapters.

a. Capable of couch and main north, sed of destroy

2. Volatilized by h

.vinite tieft and

Book II. Division I.

4

#### CHAP. I.

#### OF VOLATILE ALKALIES.

Origin.

The word ALKALT is of Arabian origin, and was introduced into chemistry after it had been applied to a plant which still retains the name of *kali*. When this plant is burnt, the ashes washed in water, and the water evaporated to dryness, a white substance remains, which was called *alkali*. According to Albertus Magnus, who uses the word, it signifies *fax amaritudinis*, "the dregs of bitterness \*." Alkali may be obtained from other substances besides kali. Chemists gradually discovered that bodies differing from one another in several of their properties, had been confounded together under the same name. The word, in consequence, became general, and is now applied to all bodies which possess the following properties :

Properties.

1. A caustic taste.

2. Volatilized by heat.

3. Capable of combining with acids, and of destroying their acidity.

\* Theatrum Chemicum, ii. 470.

4. Soluble in water even when combined with carbonic acid.

5. Capable of converting vegetable blues to green. The alkalies at present known are three in number : 1. Ammonia; 2. Potash; 3. Soda.

The two last are called fixed alkalies, because they require a red heat to volatilize them; the first is called volatilealkali, because it readily assumes a gaseous form, and consequently is dissipated by a very moderate deand carbonat gree of heat.

The fixed alkalies belong to a succeeding Chapter; the only volatile alkali at present known, namely, ammonia, shall be described in the present.

SECT. I.

OF AMMONIA.

AMMONIA can be exhibited in a state of purity only under the form of a gas. It may be procured in the following manner :

1. Put into a retort a mixture of three parts of quick- Preparalime and one part of sal ammoniac in powder. Plunge the beak of the retort below the mouth of a glass jar filled with mercury, and standing inverted in a basin of mercury. Apply the heat of a lamp to the retort : a gas comes over, which displaces the mercury and fills the jar. This gas is ammonia.

Ammonia was altogether unknown to the ancients; History. the alchymists were acquainted with it, though not in

tion.

Fropertie

bollage

Chap. I.

Book II. Division I. a state of purity, being combined with carbonic acid, and often also dissolved in water. Basil Valentine describes the method of obtaining it. It was known by the name of volatile alkali; it was also called bartsborn, because it was often obtained by distilling the horn of the hart; spirit of urine, because it may be obtained by the same process from urine; and spirit of sal ammoniac; because it may be obtained from that salt. Dr Black first pointed out the difference between ammonia and carbonate of ammonia, or ammonia combined with carbonic acid; and Dr Priestley discovered the method of obtaining it in a state of purity, by the process described in the beginning of this Section.

Properties.

2. Ammonia in the state of gas is transparent and colourless like air; its taste is acrid and caustic like that of the fixed alkalies, but not nearly so strong, nor does it like them corrode those animal bodies to which it is applied: its smell is remarkably pungent, though not unpleasant when sufficiently diluted. Its use as a stimulant to prevent fainting is well known.

Animals cannot breath it without death. When a lighted candle is let down into this gas, it goes out three or four times successively; but at each time the flame is considerably enlarged by the addition of another flame of a pale yellow colour, and at last this flame descends from the top of the vessel to the bottom \*.

Its specific gravity, according to the experiments of Kirwan, is 0.600, that of air being 1.00<sup>+</sup>. While Mr Davy found it 0.5505<sup>±</sup>. Messrs Allen and Pepys

Tas contes over, w

the jar.

\* Priestley, is 381. † On Phlogiston, p. 28. ‡ Kessarsbes, p. 565.

lately found it 0.6022\*. At the temperature of 60°, a <u>Chap.1.</u> hundred cubic inches of this gas weigh, according to Kirwan, 18.16 grains, according to Davy, 17.068, according to Allen and Pepys, 18.67. Hence it is to common air nearly as 3 to 5.

When exposed to a cold of  $-45^\circ$  it is condensed into a liquid, which again assumes the gaseous form when the temperature is raised  $\ddagger$ . When passed through a red hot tube of porcelain or glass, it is totally decomposed and converted into hydrogen and azotic gas  $\ddagger$ . That this experiment may succeed, the diameter of the tube must not be too great.

3. It combines very rapidly with water. When a bit of ice is brought into contact with this gas, it melts and absorbs the ammonia, while at the same time its temperature is diminished. Cold water absorbs this gas almost instantaneously, and at the same time heat is evolved, and the specific gravity of the water is diminished. Water, by my trials, is capable of absorbing 780 times its bulk of this gas ; while, in the mean time, the bulk of the liquid increases from 6 to 10. The specific gravity of this solution is 0.900, which just accords with the increase of bulk. It is in this state that ammonia is usually employed by chemists. The term ammonia almost always means this liquid solution of ammonia in water. When heated to the temperature of about 130°, the ammonia separates under the form of gas. When exposed to the temperature o

4. Ammoniacal gas is not altered by light; but when

\* Davy on the decomposition and composition of the fixed alkalies. Phil. Trans. 1808.

+ Morveau, Ann. de Chim. xxix. 292. + Priestley, ii. 395.

73

Book II. Division I. -46° it crystallizes; and when suddenly cooled down to -68°, it assumes the appearance of a thick jelly, and has scarcely any smell \*. http://www.scarcely.any.smell \*.

It follows from the experiments of Mr Davy, that a saturated solution of ammonia is composed of

> 74.63 water 25.37 ammonia

ander branit s

the formation and

no TREET #

#### 100.00

The following TABLE, drawn up by the same ingenious chemist, exhibits the proportion of water and ammonia contained in 100 parts of liquid ammonia of different specific gravities +.

	All a restauro	and telepoord	ei sol lo
Specific gravity.	Ammonia.	Water.	n admadn.
0.9054	25.37	74.63	peroture
0.9166	22.07	77.93	schniette 1
0.9255	19.54	80.46	Anotores
0.9326	17.52	82.48	total a
0.9385	15.88	84.12	
0.9435	14.53	85.47	130 mm
0.9476	13.46	86.54	the bulk
0.9513	12.40	87.60	specific
0.9545	11.56	88.44	a subarr
0.9573	10.82	89.18	- States
0.9597	10.17	89.83	inat sum
0.9619	9.60	90.40	ener up 1915
0.9684	9.50	90.50	of ammi
0.9639	9.09	90.91	to aver
0.9713	7.17	92.83	Contraction of the

4. Ammoniacal gas is not altered by light; but when

\* Fourcroy and Vauquelin, Ann. de Chim. xxix. 289. More the set of Con said the to the

+ Davy, p. 68.

electric sparks are made to pass through it, the bulk of Chap. I. the gas is considerably increased, and it is converted into hydrogen gas and azotic gas \*. Hence it follows that ammonia consists chiefly of hydrogen and azote. By this process Berthollet converted 1.7 cubic inches of ammoniacal gas into 3:3 cubic inches +.

5. Thisgas has no effect upon oxygen gas while cold ; Action of but when a mixture of the two gases is made to pass through a red hot porcelain tube, a detonation takes place, water is formed, and azotic gas emitted. Hence we see that ammonia is partly combustible. Its hydrogen combines with the oxygen, and forms water, while the azote makes its escape in the form of a gas ‡. If the proportion of oxygen gas be considerable, nitric acid is also formed, in consequence of the combination of the azote with the superabundant oxygen §. The same decomposition and detonation take place if common air be used instead of oxygen gas.

6. Sulphur is the only one of the simple combustibles that combines with ammonia. Hydrogen produces no change upon it whatever; but phosphorus and charcoal act with considerable effect in high temperatures. inwellies minur and the tern talmanterpress and

It combines with sulphur in the state of vapour, and forms a sulphuret which decomposes water, and forms bydrogureted sulphuret of ammonia, known formerly by the name of fuming liquor of Boyle, because it was first described by that philosopher ¶. It is commonly pre-

\* Priestley, ii. 389. + Berthollet, Jour. de Phys. xuix. 176. 1 Proust, Nicholson's Journal, iii. 328. § Fourcroy, ii. 236.

Shaw's Boyle, ii. 78.

Action of electricity.

0

oxygen.

Action of simple incombustibles,

-di bili 10

Book II. Division I. pared by distilling a mixture of five parts of sal ammoniac, five parts of sulphur, and six of quicklime. It is a liquid of a red or rather deep orange colour, and exbales a fetid odour, in consequence of an excess of ammonia which it contains. Its nature was first pointed out by Berthollet \*.

Phosphorus produces no change on ammoniacal gas while cold; but when this gas is made to pass through phosphorus in a red hot porcelain tube, it is decomposed, and phosphureted hydrogen gas, and phosphureted azotic gas are formed +.

Charcoal absorbs ammoniacal gas, but does not alter its properties while cold. But when the gas is made to pass through red hot charcoal, part of the charcoal combines with it, and forms a substance known by the name of *prussic acid* 1. Inspiration we get down by the name

Of the incombustibles,

Of metals.

7. Ammonia is not acted on by azote ; but it combines rapidly with muriatic acid ; the two gases concreting into the solid salt called *muriate of animonia*.

8. Ammonia does not combine with the metals; but it changes some of them into oxides, and then dissolves them. The oxidizement is evidently in consequence of the decomposition of part of the water with which the ammonia is combined; for hydrogen gas is emitted during the solution. Copper and zink are oxidized by the action of ammonia; as are also tin and iron, though only superficially. Scarcely any of the other metals are altered by its action.

Liquid ammonia is capable of dissolving the oxides

\* Ann. de Chim. xxv. 233. † Fourcroy, ü. 237. † Schecle, ii. 183; and Clouet, Anr. de Chim. xi. 30.

of silver, copper, iron, tin, nickel, zinc, bismuth, and Chap. I. cobalt \*. When digested upon the oxides of mercury, Dissolves lead, or manganese, it is decomposed, water is formed, ides. by the union of the hydrogen of the ammonia with the oxygen of the oxides, and azotic gas is emitted +. If a considerable heat be applied, nitric acid is formed at the same time with water ‡. Several other oxides are also partly deoxidized when ammonia is poured into their solutions in acids. The ammoniacal solution of the peroxide of copper is of a fine blue colour, and, according to Sage, capable of crystallizing. When heat is applied, the ammonia is partly driven off, and partly decomposed, by the combination of its hydrogen with the oxygen of the oxide.

9. Ammonia combines readily with the peroxides of gold and silver, and forms with them two compounds, formerly known by the names of fulminating gold and fulminating silver ; because, when heated or rubbed, they explode with great violence. It combines also with the red oxide of mercury, to provide mild of boile

Fulminating gold, known also by the name of aurate Fulminaof ammonia, may be prepared by dissolving gold in nitro-muriatic acid, diluting the solution with thrice its weight of water, and then dropping in pure ammonia by little and little as long as any precipitate is formed; taking care not to add too much, because in that case part of the precipitate is again dissolved. The precipi-

ting gold,

\* It dissolves the protoxide of iron when added in excess, but only in small quantities. The peroxide of iron is insoluble in it; so is the peroxide of cobalt, according to Thenard.

State of the hears of the

He of the still and the

+ scheele.

1 Milner, Phil. Trans.-Fourcroy, v. 355.

metallic ox-

Book II. Division I. tate, which is of a yellow colour, is to be washed in pure water, dried slowly upon filtering paper, and then put into a phial : which, to prevent accidents, ought not to be corked, but its mouth covered with a linen rag or a slip of paper. This powder is fulminating gold; which is composed of five parts of yellow oxide of gold and one part of ammonia\*. The preparation of this powder is described by Basil Valentine; and its singular properties excited the attention of all succeeding chemists. Various attempts were made to account for its fulminating property, but without success, till Bergman published his dissertation on it in 1769. He demonstrated, that it is a compound of ammonia and yellow oxide of gold : that during its explosion the oxide is reduced, the ammonia decomposed, and the azote, which it contained, set at liberty in the form of gas +. These facts (partly discovered by Scheele) led him to explain the explosion as follows : Ammonia is composed of azote and phlogiston. When heat is applied to fulminating gold, the phlogiston combines with the oxide, and forms gold, while the azote flies off in the form of gas. The experiments of Bergman and Scheele were repeated and confirmed by Berthollet in 1786; and the nature of oxides having been previously ascertained by Lavoisier, he was enabled to give a more satisfactory explanation of the phenomenon. During the explosion, the hydrogen of the ammonia combines with the oxygen of the oxide, and forms water; the gold is reduced, and the azote evolved in the form of

\* Bergman, ii. 155.

+ Bergman, ii. 153; and Scheele on Fire, p. 137.

gas. The great expansibility of this gas by heat explains the violence of the explosion.

Fulminating gold explodes when struck violently, or when triturated in a mortar, or when heated to a temperature between 248° and 54°. The noise is tremendous; and when in any considerable quantity (12 grains for instance) it lacerates the metallic plate on which it is placed. When heated in close vessels, sufficiently strong to resist its action, it is reduced silently, and without any marks of violence\*. Its force was compared with that of gunpowder by the Royal Society, but found inferior.

Fulminating silver was discovered by Berthollet in 1788. It may be formed by dissolving very pure silver in nitric acid, and then precipitating it by lime water. The precipitate is put upon filtering paper, which absorbs the water and the nitrate of lime with which it was mixed; then pure liquid ammonia is poured upon it, and allowed to remain for 12 hours ; it is then decanted off, and the black powder, on which it stood, is placed cautiously, and in very small portions, upon bits of filtering paper. This powder is fulminating silver. Even while moist it explodes with violence when struck by a hard body. When dry, the slightest touch is sufficient to cause it to fulminate. When the liquid decanted off this powder is heated in 'a glass retort, an effervescence takes place, azotic gas is emitted, and small crystals make their appearance, which are opaque, and have a metallic brilliancy. These fulminate when

\* Bergman, ii. 141.

Fulminating silver.

13

Chap. 1.

Book II. Division I.

Ammoniacal fulmina-

ting mercury. touched, even though covered by the liquid, and often break in pieces the vessels in which they are kept \*.

The theory of this dangerous powder is the same as that of fulminating gold. It is a compound of ammonia and oxide of silver. Friction, or the application of heat, occasions the combination of the oxygen of the oxide with the hydrogen of the ammonia; water is formed, the silver is reduced, and azotic gas emitted.

Ammoniacal fulminating mercury was lately discovered by Fourcroy. It may be formed by digesting a strong solution of ammonia in water upon the red oxide of mercury. After the process has continued for eight or ten days, the oxide assumes a white colour, and is at last covered with small crystalline scales. In this state it detonates loudly upon ignited coals in the same manner as fulminating gold. It loses its fulminating property, and undergoes spontaneous decomposition, in a few days. When exposed to a low heat, the ammonia is driven off, and the red oxide assumes its former appearance +.

Composition of ammonia. As ammonia has the property of detonating with nitre, chemists had unanimously agreed that it contains phlogiston. Scheele first demonstrated, that when it is decomposed by means of the oxides of manganese, arsenic, or gold, azotic gas is set at liberty, while the oxide is reduced ‡. Hence he concluded, that it is composed of azote and phlogiston; and Bergman coincided with him in opinion. Dr Priestley discovered, that

- \* Berthollet, Ann. de Chim. i. 54.
- + Journals of the Royal Institution, i. 256.
- \$ Scheele, i. 95 and 155. French Trans .- Scheele on Fire, p. 13%.

when electric explosions are made to pass through this gas, its bulk is gradually augmented to thrice the space which it formerly occupied; and a quantity of hydrogen gas is produced. The same ingenious philosopher applied heat to the red oxides of mercury and lead confined in ammoniacal gas. The oxides were reduced, water was evolved, the ammoniacal gas disappeared, and instead of it, there was found a quantity of azotic gas\*. These experiments, and those of Scheele, led to the conclusion, that ammonia is composed of azote and hydrogen; a conclusion which was fully established by the experiments of Berthollet, published in the Memoirs of the French Academy for 1785. This acute philosopher repeated the experiments of Scheele and Priestley, and applied to them the theory of Mr Lavoisier, and added also several very decisive ones of his own. The most important of these is the mutual decomposition of ammonia and oxymuriatic acid. When solutions of these bodies in water are mixed together, an effervescence takes place, azote is disengaged, a quantity of water formed, and the oxymuriatic acid is converted into common muriatic acid. Now the substances mixed were ammonia and oxymuriatic acid, which is composed of oxygen and muriatic acid; the products were, muriatic acid, azote, and water, which is composed of oxygen and hydrogen. The oxygen of the water was furnished by the acid; the other products must have been furnished by the ammonia, which has disappeared. Ammonia, therefore, must be composed of azote and hydrogen. It follows from Mr Ber-

\* Priestley, ii. 396.

6. 12.

4 P.M. Tenne, 1768.

Chap. I.

Book II. Division I. thollet's experiments, that ammonia is composed of 121 parts of azote and 29 of hydrogen \*. According to Dr Austin's calculation it is composed of 121 parts of azote and 32 of hydrogen t. Hence 100 parts of ammonia are composed of about 80 parts of azote and 20 of hydrogen. The experiments of Berthollet have been still farther confirmed by those made more lately by Mr Davy 1. and indeed were acceded to by all chemists as unexceptionable and decisive. But the unexpected discovery by Mr Dawy, that the fixed alkalies are metallie oxides, led that illustrious chemist to suspect that ammonia also might contain oxygen in so small a proportion as to escape notice. The possibility of this notion was not to be doubted, as when ammonia was decomposed by means of electricity or heat, the oxygen though present might combine with hydrogen, and form so small a quantity of water as to remain invisible among the gases evolved. A set of experiments made on purpose to ascertain the point, soon convinced Mr Davy that oxygen is actually present in this alkali. When pure dry ammoniacal gas was passed over red hot iron wire confined in a platinum tube, the iron was slightly oxydized, and a little moisture was deposited. This experiment rendered the presence of oxygen in ammonia somewhat probable; but it cannot be considered as conclusive, unless we could be certain that all common air was effectually excluded; which it is very diffi-

\* Berthollet determined the component parts of ammonia by decomposing it by electricity, and exploding the new gas with oxygen. Jour. de Phys. xxix. 177.

+ Phil. Trans. 1788, p. 386.

‡ Researches, p. 56.

cult to accomplish. When dry pure ammoniacal gas Chap. L. was decomposed in a glass tube by means of electricity, 60 measures were converted into 108 measures; consisting of 80 measures of hydrogen, and 28 of azote. Now 60 cubic inches of ammonia, if we take the ex- Ammonia periments of Allen and Pepys as our standard, weigh oxygen. 11.2 grains, while the weight of

Grains.

10.55

80 inches of hydrogen is 1.93 or at most 2.08 

#### 10.23

Grains.

So that there is a deficiency, according to the first estimate of nearly 1 grain, and according to the second of 0.65 grain. Now this deficiency can only be accounted for by supposing a little water to have been formed during the electrization, and consequently that ammonia contains a little oxygen \*:

This experiment is equally favourable to the notion, that oxygen is one of the constituents of ammonia; but before it can be relied on as decisive, we must suppose it to have been performed with a degree of accuracy scarcely conceivable, when minute portions of gaseous fluids come under examination. The following very extraordinary experiment, however, first made by Messrs Berzelius and Pontin, and afterwards repeated and improved by Mr Davy, appears to me to prove the presence of oxygen in ammonia in a very decisive manner.

Mercury, at the negative end of a galvanic battery, gas it becomes coated with muriate of ammonia, and a

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\* Davy on the Decomposition and Composition of the Fixed Alkalies. Phile Trans. 1808. Anterest of year all the abom stamatts IIA Vol. 11.

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Book II. Division I.

Its base is a metal.

is placed in contact with a solution of ammonia, and the circuit completed. It gradually increases in volume, and when expanded four or five times its former bulk, becomes a soft solid. The experiment is easier, and the amalgam more permanent, if sal ammoniac slightly moistened be substituted for liquid ammonia. Mr Davy made a cavity in a piece of sal ammoniac slightly moistened, placed it on a plate of platinum attached to the positive end of the galvanic battery, put into the cavity about 50 grains of mercury, and brought in contact with the mercury a platinum wire attached to the negative endof the battery. A strong effervescence took place, much heat was evolved, and the globule in a few minutes had enlarged to five times its original bulk, and had the appearance of an amalgam of zinc. This amalgam, at the temperature of 70° or 80°, is a soft solid of the consistence of butter; at 32° it is a firm crystallized mass. in which small facets appear, but having no perfectly. defined form. Its specific gravity is below 3. When exposed to air it soon becomes covered with a white crust of carbonate of ammonia. When thrown into water, a quantity of hydrogen is evolved equal to half its. bulk, the mercury is revived, and the water becomes a weak solution of ammonia. When confined in a given portion of air, the air increases considerably in volume,. and pure mercury re-appears. Ammoniacal gas amounting to  $1\frac{1}{3}$  or  $1\frac{3}{4}$ , the volume of the amalgam is evolved, and a quantity of oxygen equal to  $\frac{1}{2}$  or  $\frac{1}{2}$  th of the ammonia disappears. When thrown into muriatic acid gas it becomes coated with muriate of ammonia, and a little hydrogen is disengaged. In sulphuric acid it becomes coated with sulphate of ammonia and sulphur. All attempts made by Mr Davy to preserve this amal-

gam failed, owing to the impossibility of freeing it entirely of water. When put into a glass tube, or when confined under naphtha or oils, the mercury separated, ammonia was formed, and a quantity of hydrogen evolved \*.

It is obvious, from the preceding observations, that the amalgam thus formed, consisted of the basis of ammonia combined with mercury. This basis has so strong an affinity for oxygen that it immediately decomposes water, and is converted into ammonia while hydrogen is evolved. Hence appears to be the reason why hydrogen always appears during the destruction of the amalgam, and why the amalgam cannot be preserved. The quantity of basis of ammonia contained in 50 grains of mercury thus converted into a solid amalgam, it is evident from the preceding detail cannot exceed the of a grain. That so minute a portion of matter should, make so striking a change in so great a quantity of mercury, and reduce its specific gravity so enormously, is perhaps the most extraordinary fact that has yet appeared in chemistry.

Oxygen then appears to be a constituent part of ammonia; the other ingredients of it, when deprived of that principal, acquire the property of amalgamating with mercury, and of course must be of a metallic nature. This is another unexpected and extraordinary fact. What is this metal evolved from ammonia, and to which the name of *ammonium* has been given? Is it in fact composed of one or of two metals? Are *azote* 

\* Davy's Electrochemical Researches on the Decomposition of the Earths, Sc. Phil. Trans. 1808. 10

Chap. I.

Book II. Division I. and bydrogen each metals in the gaseous state, or are they metallic oxides, or do they constitute a single metal when united together? These are questions which the present state of the subject does not enable us to resolve. The experiments seem rather more favourable to the last supposition, which is the opinion entertained by Berzelius, but they are by no means capable of deciding it.

Several successful attempts have been made to form ammonia artificially. Dr Austin indeed failed in his attempts to form it by uniting together hydrogen and azotic gases by means of heat, electricity, and cold. And now that we know that this alkali is of a more compound nature than this philosopher supposed, we cannot be surprized at his failure. It could not be doubted, however, that the alkali is often formed during different chemical processes. Dr Priestley \* and Mr Kirwan + had actually produced it even before its composition was known. It had been found, that when tin is moistened with nitric acid, and after being allowed to digest for a minute or two, a little potash or lime is added, ammonia is immediately exhaled. The nitrie acid and the water which it contains are decomposed; the oxygen of each unites with the tin, and reduces it to the state of an oxide; while at the same time the hydrogen of the water combines with the azote of the acid and with some oxygen, and forms ammonia, which is driven off by the stronger affinity of the potash or lime. Dr Austin succeeded also in forming ammonia by several other methods. He introduced into a glass tube

\* On Air, ii. 41.

† On Hepatic Lir, § iik

\* Darry Material Street

#### AMMONIÁ.

filled with mercury a little azotic gas, and then put into the gas some iron filings moistened with water. The iron decomposes the water, and combines with its oxygen ; and the hydrogen, meeting with azote at the moment of its admission, combines with it, and forms ammonia. This experiment shows, that the gaseous state of the azote does not prevent the formation of ammonia. The experiment succeeded also when common air was used instead of azote, but a longer time elapsed before the extrication of ammonia became sensible. Hence it is likely that ammonia is evolved whenever iron rusts in contact with water and air 5, 913 and alls beach an

a solid state. I helt taste is usuch mone antid. Two dib and idda. They form the subject of the following

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SECT. I. AND STORES

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Chap. I.

Method of In a sufficient quantity of wood be burnt to ashen, and these ashes he afterwards washed repeatedly with water till it courses off free from any taste and if this liquid be filtrated and evaporated to dryness, the substance which remains behind is potath ; not; inowaver, in a state of . purity, for it is contaminated with several other substances, but sufficiently pure to exhibit many of its proporties. In this state it occurs in commerce under the nanie of perarb. When heated to reducts, many of its

#### FIXED ALKALIES.

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Book II. Division I.

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the extrication of ammonia became sensible.

This experiment shows, that the descus s

THE fixed alkalies are distinguished from the volatile in not being gaseous. They may be exhibited pure in a solid state. Their taste is much more acrid. Two fixed alkalies only are at present known; namely, *potasb* and *soda*. They form the subject of the following Sections.

#### SECT. I.

#### OF POTASH.

Method of procuring potash. IF a sufficient quantity of wood be burnt to ashes, and these ashes be afterwards washed repeatedly with water till it comes off free from any taste, and if this liquid be filtrated and evaporated to dryness, the substance which remains behind is *potasb*; not, however, in a state of purity, for it is contaminated with several other substances, but sufficiently pure to exhibit many of its properties. In this state it occurs in commerce under the name of *potasb*. When heated to reduess, many of its impurities are burnt off: it becomes much whiter than before, and is then known in commerce by the name of *pearl-asb*. Still, however, it is contaminated with many foreign bodies, and is itself combined with carbonic acid gas, which blunts all its properties. It may be obtained perfectly pure by the following process:

1. Mix it with twice its weight of quicklime, and ten times its weight of pure water : Boil the mixture for some hours in a clean iron vessel, or allow it to remain for 48 hours in a close glass vessel, shaking it occasionally. Then pass it through a filter. Boil the liquid obtained in a silver vessel very rapidly, till it is so much concentrated as to assume when cold the consistence of honey. Then pour upon it a quantity of alcohol equal in weight to one-third of the pearl-ash employed. Shake the mixture, put it on the fire, let it boil for a minute or two, then pour it into a glass vessel and cork it up. The solution gradually separates itself into two strata : the lowest consists of the impurities, partly dissolved in water and partly in a solid state; the uppermost consists of the pure potash dissolved in alcohol, and is of a reddish-brown colour. Decant this alcohol solution into a silver basin, and evaporate it rapidly till a crust forms on the surface, and the liquid below acquires such consistence as to become solid on cooling. Then pour the solution into a porcelain vessel. When cold, it concretes into a fine white substance, which is pure potash. It must be broken to pieces, and put into an air-tight phial.

For this process we are indebted to Berthollet \*. The

\* Jour de Pbys. xxviii. 401.

Chap. II.

Book II. Division I. following, which was first proposed by Lowitz of Pe, tersburgh, is less expensive. The potash of commerce and quicklime are to be boiled together, as above described. The filtered liquor is then to be evaporated till a thick pellicle appears on its surface, and afterwards allowed to cool; and all the crystals which have formed are to be separated, for they consist of foreign salts. The evaporation is then to be continued in an iron pot; and, during the process, the pellicle which forms on the surface is to be carefully taken off with an iron skimmer. When no more pellicle ap ears, and when the matter ceases to boil, it is to be taken off the fire, and must be constantly agitated with an iron spatula while cooling.. It is then to be dissolved in double its own weight of cold water. This solution is to be filtered and evaporated in a glass retort \* till it begins to deposite regular crystals. If the mass consolidates ever so little by cooling, a small quantity of water is to be added, and it must be heated again. When a sufficient number of crystals have been formed, the liquor which swims over them, and which has assumed a very brown colour, must be decanted off, and kept in a well-closed bottle till the brown matter has subsided, and then it may be evaporated as before, and more crystals obtained +. acquires such consistence as to becene sol

The theory of these processes is obvious: The lime separates the carbonic acid, for which it has a stronger

pure potech. It must be broken to places, and put int

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\* Dr Kennedy observes, very justly, that a glass retort ought not to be employed, because potash in this state dissolves glass. *Edin. Trans.* v. 97.

† Nicholson's Journal, i. 164.

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affinity; and the alcohol or the evaporation separate all the other foreign ingredients.

A still simpler method is employed by Klaproth. He boils equal parts of salt of tartar (carbonate of potash prepared from tartar), and carrara marble or oyster shells, burnt to lime, with a sufficient quantity of water, in a polished iron kettle. The ley is then strained through clean linen, and though still turbid, is reduced by boiling, till it contain about one half its weight of potash. It is then passed a second time through a linen cloth, and set bye in a glass bottle. After some days, when the ley has become clear of itself, it is decanted off from the sediment into another bottle \*.

As potash is never obtained at first in a state of puri- Black's disty, but always combined with carbonic acid, it was long the cause of before chemists understood to what the changes produced upon it by lime were owing. According to some, it was deprived of a quantity of mucilage, in which it had formerly been enveloped; while, according to others, it was rendered more active by being more comminuted. At last, in 1756, Dr Black proved, by the most ingenious and satisfactory analysis, that the potash which the world had considered as a simple substance, was really a compound, consisting of potash and carbonic acid; that lime deprived it of this acid; and that it became more active by becoming more simple.

While Dr Black was thus occupied in Scotland, Mr Meyer was employed in Germany in the same researches; from which, however, he drew very different conclusions. His Essays on lime appeared in 1764.

\* Klaproth's Beitrage, i. Preface, p. 10.

77.5 in his physical and chemical essays. He re-

cumed by Mr Lavoisier

covery of causticity.

Chap. II.

Book II. Division I.

Pouring into lime-water a solution of potash (earbonate of potash), he obtained a precipitate, which he found not to differ from lime-stone. The alkali had therefore deprived the lime of its causticity and its active properties; and these very properties it had itself acquired. From which he concluded, that the causticity of lime was owing to a particular acid with which it had combined during its calcination. The alkali deprived the lime of this acid, and therefore had a stronger affinity for it. To this acid he gave the name of acidum pingue or causticum. It was, according to him, a subtile elastic mixt, analogous to sulphur, approaching very nearly to the nature of fire, and actually composed of an acid principle and fire. It was expansible, compressible, volatile, astringent, capable of penetrating all vessels, and was the cause of causticity in lime, alkalies, and metals. This theory was exceedingly ingenious, and it was supported by a vast number of new and important facts. But notwithstanding the reputation and acknowledged genius and merit of its author, it never gained many followers; because the true theory of causticity, which had been already published by Dr Black, soon became known on the continent ; and notwithstanding some opposition at first, soon carried conviction into every unprejudiced mind. Mr Jacquin, botanical professor at Vienna, published a latin dissertation in defence of Dr Black's doctrine in 1769, This work was opposed in 1770 by Crans, physician to the king of Prussia, who endeavoured to defend the hypothesis of Meyer, who was now dead, in a very elaborate The subject was resumed by Mr Lavoisier treatise. in 1774 in his physical and chemical essays. He repeated the experiments of Dr Black and his disciples,

and confirmed them in every particular. Since that Chap. II. time the hypothesis of Meyer seems to have been abandoned by every one.

That potash was known to the ancient Gauls and Germans cannot be doubted, as they were the inventors of soap, which, Pliny informs us, they composed of ashes and tallow. These ashes (for he mentions the ashes of the beech-tree particularly) were nothing else but potash; not, however, in a state of purity \*. The xovia, too, mentioned by Aristophanes and Plato, appears to have been a ley made of the same kind of ashes. The alchymists were well acquainted with it; and it has been in every period very much employed in chemical researches. It may be said, however, with justice, that till Berthollet published his process in the year 1786, chemists had never examined potash in a state of complete purity †.

2. Potash is a brittle substance of a white colour, and Properties a smell resembling that which is perceived during the slacking of quicklime. Its taste is remarkably actid; and it is so exceedingly corrosive, that when applied to any part of the body, it destroys it almost instantaneously. On account of this property, it has been called

of potash.

\* Plinii lib. xviii. c. 51.

+ Potash was long distinguished by the name of vegetable alkali, because it is obtained from vegetables, and because it was long thought to be peculiar to the vegetable kingdom; but this is now known to be a mistake. It was called also salt of tartar, because it may be obtained by burning the salt called tartar. Mr Kirwan has given it the name of tartarin ; Dr Pearson has called it vegalkali ; Klaproth kali ; and Dr Black lixiva. By most British chemists it is called potasb ; but this term, in common language, signifies the carbonate of potash, or the potash of commerce.

Book II. Division I.

*caustic*, and is often used by surgeons, under the name of the *potential cautery*, to open abscesses, and to destroy useless or hurtful excrescences. Its specific gravity is 1.7085 ‡.

When heated it melts; at a red heat it swells, and evaporates slowly in a white acrid smoke. A strong heat gives it a greenish tinge, but produces no other alteration in it. Potash is not altered by exposure to light.

When exposed to the air, it soon attracts moisture, and is converted into a liquid; at the same time it combines with carbonic acid, for which it has a strong affinity.

Its combination with water. 3. It has a very strong affinity for water. At the common temperature of the air, one part of water dissolves two parts of potash. The solution is transparent, very dense, and almost of the consistence of oil. It is in this state that potash is usually employed by chemists. When four parts of potash in powder and one of snow are mixed together, the mixture becomes liquid, and at the same time affords a quantity of caloric. This mixture was employed by Lowitz to produce artificial cold. When the aqueons solution of potash is evaporated to a proper consistency, the potash crystallizes. The shape of its crystals is very different, according to the way in which they have been produced. When allowed to form spontaneously, they are octahedrons in groupes, and contain 0.43 of water \*: When formed by evaporation

‡ Hassenfratz, Ann. de Chim. xxviii. 11.

• According to Proust, the hydrate of potach contains only 0.30 of water. Jour. de Phys. lix. 266.

to the Person has called it event to

on the fire, they assume the figure of very thin transparent blades of extraordinary magnitude, which, by an assemblage of lines crossing each other in prodigious numbers, present an aggregate of cells or cavities, commonly so very close, that the vessel may be inverted without losing one drop of the liquid which it contains t.

4. Potash shows no disposition to unite with oxygen, Action on neither is it altered by the action of any of the compounds into which oxygen enters, though it has a strong tendency to unite with several of these compounds.

5. It unites with none of the simple combustibles ex- On simple cept sulphur. Carbon and hydrogen do not act upon it bles. at all; neither does it produce any alteration in them, but it acts upon phosphorus with considerable energy.

When three parts of sulphur and one of potash are Sulphuret triturated together in a glass mortar, the sulphur acquires a green colour, the mixture becomes hot, and exhales an alliaceous odour. It gradually attracts moisture from the air, and is totally soluble in water \*. When two parts of potash and one of sulphur are heated in a crucible, they melt and combine, and form a sulphuret of potash. The potash of commerce may be also employed; for the carbonic acid separates in the form of a gas during the combination of the potash and sulphur. When the fusion is complete, the sulphuret is to be poured upon a marble slab; and as soon as it congeals, it must be broken in pieces, and set by in a welleorked phial.

Sulphuret of potash, thus prepared, is of a brown co-

+ Nicholson's Journal, i. 164. \* Fourcrey, ii. 293.

oxygen,

combusti-

of potash.

Consul-

Chap. II.

Book II. Division I. lour, not unlike the liver of animals. Hence it was formerly called *bepar sulphuris*, " liver of sulphur;" but when exposed to the air, it soon becomes green, and even white. It is hard, brittle, and has a glassy fracture. Its taste is acrid, caustic, and bitter, and it leaves a brown stain upon the skin. It has no other smell than that of sublimed sulphur. When exposed to a violent heat, the sulphur sublimes, and the potash remains in a state of purity. This sulphuret converts vegetable blues to green, and soon destroys them. When heated with charcoal, it dissolves and combines with it<sup>\*</sup>.

When sulphuret of potash is exposed to the air, or when it is moistened with water, its properties very soon change. It acquires a green colour, and exhales the odour of sulphureted hydrogen gas. This change is owing to the formation of a quantity of sulphureted hydrogen, in consequence of the decomposition of the This new-formed substance combines with the water. sulphuret, and converts it into bydrogureted sulphuret of potasb, which is soluble in water, and has a brownish green colour. It may be formed also by boiling in water two parts of potash and one part of sulphur. Sulphuret of potash produces no change upon air, but hydrogureted sulphuret gradually absorbs oxygen. When inclosed in a vessel with a quantity of air, it soon absorbs all the oxygen of that portion, and leaves nothing but azotic gas. This fact, which was first observed by Scheele, induced him to use hydrogureted sulphuret to measure the quantity of oxygen contained in any given

\* Fourcroy, ii. 203-

Hydrogureted sulphuret. portion of atmospheric air. Hydrogureted sulphuret is Chap. II. capable of oxidizing and dissolving almost all the metals. We are indebted to Mr Berthollet for the first accurate account of the difference between these two substances +.

Potash cannot be combined with phosphorus by any Action on method at present known. But when potash, dissolved phosphorus. in water, is heated over phosphorus in a retort, the water is gradually decomposed, part of the phosphorus is converted into phosphoric acid, and a great quantity of phosphureted hydrogen gas is emitted, which takes fire, as usual, as soon as it comes in contact with the air of the atmosphere. It was by this process that Gengembre first obtained phosphureted hydrogen gas.

6. It does not appear that potash is capable of uniting Action on with azote, or even of acting on it at all: but with combustimuriatic acid it unites very readily, and forms the com- bles, pound known by the name of muriate of potash.

7. Potash does not combine with any of the metals; On metals, but some of the metals which have a strong affinity for oxygen, when put into a solution of potash in water, especially if heat be applied, are gradually oxidized. This is the case with molybdenum, zinc, and iron. Tin also is oxidized in a very small proportion; and this seems also to be the case with manganese.

It is capable of dissolving a considerable number of And their the metallic oxides; and in some cases it deprives them oxides. of a dose of their oxygen. Thus when poured upon the red oxide of iron, it soon converts it into the black. The cause of this change is unknown. It has been as-

f Ann. de Chim. xxv. 233. See also Proust, Jour. de Phys. lix. 265.

simple in-

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We are indebird to Mr. Berthollet for my first an-

certained, that the oxides of the following metals are so-Book II. Division I. luble in potash : and gate lot in her prividize to alderes

> - Gut U Lead \*, deputed pourte L Zinc, o foureau alenna Tin, Manganese,

> Antimony, Nickel, Tellurium, Arsenic, Tungsten, Cobalt, Molybdenum.

But the nature of these solutions has not hitherto been examined with any degree of attention; though the subject is remarkably curious, and promises to throw light both upon the nature of alkalies and metals.

Whether a sompound.

Various opinions have been entertained by chemists respecting the composition of potash. At one time it was fashionable to consider azote as one of its constituents; because that principle had been detected in ammonia, and it was thought not unlikely by Lavoisier, that as oxygen, one of the constituents of air, was the acidifying principle, azote, the other constituent, would be found to be the principle of alkalisation. Morveau and Desormes announced, some time ago, that they consider potash as a compound of hydrogen and lime. Their chief proofs were the appearance of lime, when the salt, composed of hyperoxygenized muriatic acid and potash, is strongly heated with phosphoric acid in a crucible of platinum; and a manifest combustion, together with the deposition of lime, when charcoal and potash are in like manner exposed to a strong heat in a

\* Bergman, iii. 456. Proust, Jour. de Phyr. lvi. 207.

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## FOTASH.

platinum crucible \*. But these and the other experimen. Chap. II. tal proofs being examined by Darracq, that accurate chemist ascertained that the results obtained by Desormes and Morveau were owing, in most cases, to the impurity of the potash with which they had made their experiments; while in others they had drawn wrong inferences from mistaken resemblances +. Their hypothesis of course cannot be maintained.

This question, inferior to none in the annals of che- Composimistry, has been at last decided by the happy sagacity of Mr Davy, who has recently enriched chemistry with a long train of the most important and brilliant discoveries. Potash, it follows from his experiments, is a compound of oxygen and a new metal, to which he has given the name of potassium.

When potash is perfectly dry it is a non-conductor of How deelectricity, but it becomes a conductor when slightly moistened on the surface, a degree of moisture which it acquires by being exposed for a few seconds to the atmosphere. When pieces of potash in this state are placed upon a disc of platinum attached to the negative end of a powerful galvanic battery, and a platinum wire from the positive extremity is made to touch its upper surface, the potash is gradually decomposed, oxygen gas separating at the extremity of the positive wire, while globules of a white metal like mercury appear at the side in contact with the platinum disc. A number of accurate experiments demonstrated to Mr Davy, that these globules were the basis of potash, and that they were converted into potash by absorbing

\* Mem. de l' Instit. iii. 322. Vol. II.

+ Ann. de Chim, xl. 171. C

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Properties

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Book II. Division I.

Properties of potasanm.

Its specific gravity.

Action of oxygen.

-55 Wolff

oxygen. This metallic substance possesses the following properties : da poerted and bening a select above lat

Its colour is white like that of mercury. At the temperature of 100° it is as fluid as mercury ; at 60° it still continues imperfectly fluid; at 50° it is a soft and malleable solid, while at 32° it is hard, brittle, and crystallized in facets. When heated nearly to redness it is volatilized and converted into vapour. It conducts electricity and heat as well as other metallic bodies.

> It differs remarkably from all the metals previously known in its specific gravity; being lighter than any other liquid substance hitherto examined, swimming even in naphtha of the specific gravity 0.770. As it alters very rapidly when exposed to the air, it is difficult to ascertain its specific gravity with accuracy. Mr Davy endeavoured to estimate the relative weight of a globule of potassium and of mercury, of exactly the same bulk, measured by means of a micrometer : he found the weights to each other as 10 to 223, which gives 0.6 nearly for the specific gravity of potassium.

> Its affinity for oxygen and its tendency to absorb that principle are much greater than that of any other substance previously known. Hence, if exposed to the air, it absorbs oxygen, and is covered with a crust of potash in a few minutes; this crust absorbs water which is rapidly decomposed, and in a short time the whole becomes a saturated solution of potash. When thrown upon water it decomposes that liquid with rapidity, heat is evolved, hydrogen gas holding potassium in solution is emitted, which takes fire spontaneously, and the whole potassium burns with an explosion, and is converted into potash. It burns equally when placed upon ice. It equally decomposes water, and is converted in-

> > Vol. 11

to potash when kept in alcohol, ether, and oils, or when thrown into the mineral acids. Newly distilled naphtha is the substance in which it may be best preserved. In this liquid it remains unaltered for many days, and may be readily examined in the open air when covered with a crust of it.

When heated in hydrogen gas, a portion of it is dissolved, and the gas acquires the property of burning spontaneously when it is mixed with atmospheric air. But if kept for a short time it again deposites the potassium, and loses the property of burning spontaneously.

When heated in a small quantity of oxygen gas it ab- Protoxide sorbs a portion of it, loses its metallic appearance, as- of potassumes a reddish brown colour, and becomes grey when cold. In this state it may be considered as a protoxide of potassium. This protoxide may be readily formed by fusing together potash and potassium in a glass tube filled with the vapour of naphtha. When exposed to the air it readily absorbs more oxygen, and is converted into potash.

When potassium is exposed to the action of oxymuriatic acid gas it takes fire, and is converted into muriate of potash.

Potassium, when brought in contact with phosphorus, phosphuret, and pressed upon under naphtha, combines with it and forms a phosphuret of potassium, which has the colour of lead, and remains solid at the boiling point of naphtha. When exposed to the air it slowly absorbs oxygen and is converted into phosphate of potash. When the metal and phosphorus are brought into contact in the open air, they become fluid together, burn, and are converted at once into phosphate of potash.

C 2

Chap. II.

Book II. Division I. Sulphuret. Potassium combines rapidly with sulphur in tubes filled with the vapour of naphtha, while heat and light are evolved. The sulphuret formed has the grey colour of artificial sulphuret of iron. A little sulphureted hydrogen is given out during the formation of this compound. In the open air the combination takes place with combustion, and sulphuret of potash is formed. Sulphuret of potassium, when exposed to the air, is gradually converted into sulphate of potash.

Alloys.

Potassium readily combines and forms an alloy with all the metals hitherto tried. When one part of potassium is added to about 10 parts of mercury in bulk, they instantly unite and form a substance very like mercury in colour. When a globule is made to touch a globule of mercury twice as bulky, they combine with considerable heat. The globule is at first fluid, but on cooling becomes solid and resembles silver. If the potassium be increased to about Toth of the mercury inweight, the amalgam is harder and becomes brittle. One part of potassium renders 70 parts of mercury solid, and forms an amalgam very soft and malleable. When these amalgams are exposed to the air, they rapidly absorb oxygen, potash is formed, which deliquesces, and in a few minutes the mercury is found pure and unaltered. In water the amalgam is decomposed with a hissing noise, hydrogen gas is evolved, and the mercury remains free. The fluid amalgam of potassium acts, upon most metals. In this state of union mercury acts on iron and platinum.

When potassium is heated with gold, silver, or copper in a close glass vessel, it combines with them. The alloy is decomposed when thrown into water, potash is formed, and the other metals separated. No attempts

#### POTASH.

have been made to combine it with other metals, except with fusible metal, with which it unites and forms an alloy that requires more heat to melt it than the fusible metal itself.

When potassium is mixed and heated with metallic oxides, it rapidly reduces them to the metallic state. Mr ides. Davy tried the experiment on the oxides of iron, tin, and lead. When there is an excess of potassium it forms an alloy with the revived metal. Its action upon metallic oxides is so strong, that it readily decomposes flint and green glass in a gentle heat. Is not hap bet to tree

Mr Davy demonstrated by the most decisive experiments, that when potassium combines with oxygen to saturation it is converted into potash. He performed this experiment in glass tubes, and ascertained the bulk of oxygen gas absorbed during the combustion of a given weight of potassium. From these experiments it follows, that potash is composed of about 6 parts potassium and 1 part of oxygen, or nearly of southoo but

potassium 86 .... Juli .... yvs T ber sienenthe stille oxygen to 14 story off the man azote. The fast comprend h fantise spontime and y

vater exposed to the in his his his a Galvanism is not the only mode by which potash may Potash debe decomposed, and its base obtained nearly in a state by iron. of purity. Gay Lussac and Thenard have succeeded in decomposing it by means of iron filings; and their experiment has been successfully repeated by Mr Davy. Into the middle of an iron gun barrel is to be put a quantity of clean and dry iron filings or turnings. An iron tube, containing potash as dry as possible, should be ground to one end of the gun barrel, and having a

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compose

Constituents of potash.

Chap. It.

Action on metallic ox-

37

Book If. Division I. small hole through which the potash may run slowly when melted. To the other extremity a tube of safety, containing mercury or naphtha, ought also to be luted, and great care should be taken that all the lutings be air tight. The gun barrel being laid across a furnace, the iron turnings within it are brought to a white heat, while the potash is kept cool by means of ice; then the potash is brought into fusion, and made to flow slowly through the iron turnings. Hydrogen gas is emitted in considerable quantity during the whole process. The part of the gun barrel next the tube of safety should be kept constantly cool. When the process is at an end, a portion of potassium nearly pure is found near the tube safety; but the greatest part of it is alloyed with the iron turnings \*.

Such are the properties of potassium hitherto investigated. For all the facts above stated we are indebted to Mr Davy  $\dagger$ ; but his experiments have been repeated and confirmed by other respectable philosophers. Mr Davy has lately ascertained that the protoxide of potassium has the property of combining with ammonia and azote. The last compound inflames spontaneously when exposed to the air, potash is formed, and azotic gas disengaged. It acts violently on water, and produces potash and ammonia  $\ddagger$ .

Potash or the peroxide of potassium is of the highest

ine des omplasting for hy mesons loft if on offinger, and the beexperiment her before a successfully sequented by Mr Davy. Into the middle of an iron gast hersel is to be put a

\* Pbil, Mag. xxxii. 89; and 276. See also a note in Mr Davy's paper Cu the Decomposition of the Easths. Phil. Trans. 1808.

See Davy's lecture on the Decomposition and Composition of the Fixed Malaties. P . Trans. 1809.
Phil, Mag. XXXII. 368

importance, not only in chemistry, where it is employed for a great variety of purposes, but also in many arts and manufactures; as washing, bleaching, dyeing, glass-making, and others, as will afterwards appear. It is employed also in surgery and medicine.

and several other lowing ing shares buy it may be ab-

tained perfectly pure by bi

shada and potadi recomble cach other so matches that -tailing and sec SECT. II. ed his discription on common sale in the Menous of

OF SODA.

rise base of common safe is solder and thus

SODA, called also fossil or mineral alkali\*, because it Names. was thought peculiar to the mineral kingdom, was known to the ancients (though not in a state of purity) under the names of vileov and nitrum +.

It is found in large quantities combined with carbonic acid in different parts of the earth, especially in Egypt; and common salt is a compound of soda and muriatic acid. But the soda of commerce is obtained from the ashes of different species of the salsola, a genus of plants which grow upon the sea-shore, especially from the salsola soda, from which the alkali has obtained its name. The soda of commerce is also called barilla, because the plant from which it is obtained bears that name in Spain. Almost all the algæ, especially the nor desert combine with 6xypten in draged, anote, clu-

\* Dr Pearson has proposed to distinguish it by the name of fossalkali; Klaproth calls it natron.

han altered but metals. Its attion under their bords and actioner if the same which that we potestic The

+ The Alpow of the Athenians was evidently the same substance ; and so was the nn of the Hebrews.

Preparation.

Properties.

30

Chap. II.

Book II. Division I. fuci, contain also a considerable quantity of soda. The ashes of these plants are known in this country by the name of *kelp*; in France they are called *varec*.

The soda, or barilla, of commerce, is far from being pure; besides carbonic acid it contains common salt, and several other foreign ingredients; but it may be obtained perfectly pure by the processes described in the last Section for purifying potash.

Soda and potash resemble each other so nearly, that they were confounded together till Du Hamel published his dissertation on common salt in the Memoirs of the French Academy for 1736. He first proved that the base of common salt is soda, and that soda is different from potash. His conclusions were objected to by Pott, but finally confirmed by Margraff in 1758 \*.

Properties.

Section 20

Soda is of a greyish-white colour, and agrees exactly with potash in its taste, smell, and action upon animal bodies; but its specific gravity is only 1.336 <sup>+</sup>.

Heat produces on it exactly the same effects as upon potash. When exposed to the air, it absorbs moisture and carbonic acid, and is soon reduced to the consistence of paste: but it does not liquefy like potash; in a few days it becomes dry again, and crumbles into powder.

It has a strong affinity for water, dissolves in it like potash, and may also be obtained in crystals by evaporating its aqueous solution. It is not altered by light; nor does it combine with oxygen, hydrogen, azote, carbon, charcoal, nor metals. Its action upon phosphorus and sulphur is the same with that of potash. The sul-

\* Opusc. ii. 331.

a strength Ly good

† Hassenfratz, Ann. de Chim. xxviii. II.

phuret and hydrogureted sulphuret of soda possess the properties of the sulphuret and hydrogureted sulphuret of potash, and are formed in the same manner. In its action on metals, metallic oxides, and in its affinities, it also agrees with potash. In short, the two fixed alkalies, in a state of purity, resemble each other very nearly in almost every particular.

Similar opinions respecting its composition were entertained by chemists, as those which they had respecting the composition of potash. Fourcroy supposed it a compound of magnesia and azote. Desormes and Morveau\*, on the other hand, affirmed that it is composed of magnesia and hydrogen; but the experiments upon which this opinion was founded have been proved inaccurate by Darracq +. Mr Davy has lately succeeded in decomposing it by the same processes which enabled him to ascertain the composition of potash. Like that alkali it is a metallic peroxide. To its metallic basis Mr Davy has given the name of sodium.

Soda is decomposed by the galvanic battery in the same way as potash; but requires a more powerful battery, or much smaller pieces of soda must be exposed to its action.

Sodium is a white metal like silver, and at the com- Properties mon temperature of the atmosphere is solid; but exceedingly malleable, and so soft that pieces of it may be welded together by strong pressure. It still retains its malleability and softness at the temperature of 32°. When heated to 120° it begins to melt, and is completely fluid at 180°; though exposed to a red heat

obtain contact while a small provide of wmer.

of sodium.

Chap. Il.

Composition.

Mem. de l'Instit. iii. 321.

† Ann. de Chim. 11. 171.

41

Book II. Division I. strong enough to melt plate glass, none of it is volatilized.

It conducts electricity and heat in the same manner as potassium. It is heavier than that metal, though not so heavy as water; swimming in oil of sassafras, of the specific gravity 1.006, and sinking in naphtha of the specific gravity 0.861. By mixing these two liquids together till they acquired just the specific gravity of sodium, Mr Davy ascertained that the specific gravity of that metal is 0.9348.

Its affinity for oxygen is similar to that of potassium, and hence it acts nearly in a similar manner when exposed to substances containing that principle. When exposed to the air it absorbs oxygen, and is soon covered with a crust of soda, which deliquesces much more slowly than potash; hence the sodium is not so soon converted into an alkali as potassium. No combustion takes place unless the sodium is heated nearly to redness; but the rapidity of the absorption of oxygen increases with the temperature. The flame which it produces in oxygen gas is white, and as it sends out bright sparks the effect is beautiful.

Hydrogen gas though assisted by heat seems to have no action on it whatever. When thrown into water sodium occasions a violent effervescence, with a loud hissing noise; hydrogen gas is evolved and soda formed; but no combustion takes place as happens to potassium, probably because sodium is insoluble in hydrogen gas. A few scintillations indeed appear when sodium is thrown into hot water. Sodium usually burns also when brought in contact with a small particle of water, or when placed on moistened paper.

Trotoxide.

When fused with dry soda in certain quantities, there

is a division of oxygen between the soda and the base ; and a protoxide of sodium is formed of a deep brown colour while fluid, but which becomes a dark grey solid on cooling. This protoxide when exposed to the air absorbs oxygen, and is converted into soda.

When sodium is exposed to the action of oxymuriatic acid gas, it burns vividly with bright scintillations of a red colour.

It combines with phosphorus with the same pheno- Phosphumena as potassium, and forms a similar phosphuret, which is converted into phosphate of soda by exposure Thus it appears that both the fixed alkalies a.ris oft ot

It combines with sulphur in close vessels filled with Sulphuret. the vapour of naphtha with great vividness, with light and heat, and often with explosion from the vaporization of a portion of the sulphur, and the disengagement of sulphureted hydrogen. The sulphuret of sodium is 

It decomposes the water in alcohol and ether precisely as potassium does. In oils it gradually absorbs oxygen and forms soaps. It is converted into soda when thrown into the mineral acids, in nitric acid with inflammation, and in sulphuric and muriatic acids with the evolution of much heat.

It combines with metals, and forms alloys similar to Alloya the alloys of potassium. One part of it renders 40 parts of mercury solid, and of the colour of silver ; and the combination is attended with a considerable degree of heat. It combines with tin without changing its colour, and acts on gold and lead by the assistance of heat. When these alloys are exposed to the air the sodium soon absorbs oxygen, and is converted into soda;

Chap. Il.

ret.

Book II. Division I.

Composition of soda. the amalgam of sodium combines with the other metals and with sulphur, forming triple compounds.

From a number of experiments on the combination of sodium with oxygen, made in the same manner as those on the combination of potassium with the same principle, Mr Davy has shown that soda is composed of about 7 parts sodium and 2 of oxygen, or nearly of

Sodium 78 Sodium

mena as potassium, a<del>nd f</del>orns a sitelite phospheter. which is converted into phosphate of soda by expecte

Thus it appears that both the fixed alkalies are metallic peroxides, and that the bases of both are capable of combining with two doses of oxygen. But the protoxide is not permanent in consequence of its great affinity for oxygen.

The importance of soda in manufactures is not inferior to that of potash. For several purposes, indeed, as for the manufacture of soap and glass, it answers even better than potash.

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## ALKALINE EARTHS.

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Chap. III.

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THE word EARTH, in common language, has two meanings; it sometimes signifies the globe, which we inhabit, and sometimes the mould on which vegetables grow. Chemists have examined this mould, and have found that it consists of a variety of substances mixed together without order or regularity. The greatest part of it, however, as well as of the stones which form apparently so large a proportion of the globe, consists of a small number of bodies, which have a variety of common properties. These bodies chemists have agreed to class together, and to denominate earths.

Every body which possesses the following properties is an earth.

1. Insoluble in water, or nearly so; or at least beco- Properties. ming insoluble when combined with carbonic acid.

2. Little or no taste or smell; at least when combined with carbonic acid.

3. Fixed, incombustible, and incapable while pure of being altered by the fire.

4. A specific gravity not exceeding 4.9.

## ALKALINE EARTMS.

Book II. 5. When pure, capable of assuming the form of a Division I. white powder.

6. Not altered when heated with combustibles.

The earths have been divided into two classes, namely, alkaline earths and earths proper. The first have the property of giving a green colour to vegetable blues, and of neutralizing acids; the second do not alter vegetable blues, and are incapable of neutralizing acids.

The alkaline earths are four in number ; namely,

LIME, MAGNESIA, BARYTES, STRONTIAN.

The properties of these bodies occupy our attention in the four following Sections.

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LIME has been known from the earliest ages. The ancients employed it in medicine; it was the chief ingredient in their mortar; and they used it as a manure to fertilize their fields.

Lime abounds in most parts of the world, or perhaps I should rather say, that there is no part of the world where it does not exist. It is found purest in limestones, and marbles, and chalk. None of these substances, however, is, strictly speaking, lime; but they are all capable of becoming lime by a well-known process, by keeping them for some time in a white heat : this process is called the burning of lime. The product, which in common language is denominated quicklime, is the substance known in chemistry by the name of lime.

1. Lime may be obtained perfectly pure by burning Preparathose crystallized limestones, called calcareous spars, which are perfectly white and transparent, and also by burning some pure white marbles. It may be procured also in a state of purity by dissolving oyster-shells in muriatic acid, filtering the solution, mixing it with ammonia as long as a white powder continues to fall, and filtering again. The liquid is now to be mixed with a solution of carbonate of soda : the powder which falls being washed and dried, and heated violently in a platinum crucible, is pure lime.

2. Pure lime is of a white colour, moderately hard, properties. but easily reduced to a powder.

It has a hot burning taste, and in some measure corrodes and destroys the texture of those animal bodies to which it is applied. Its specific gravity is 2.3\*. It tinges vegetable blues green, and at last converts them to yellow.

It is incapable of being fused by the most violent heat that can be produced in furnaces, or even by the most powerful burning-glasses.

3. If water be poured on newly burnt lime, it swells Slacking of and falls to pieces, and is soon reduced to a very fine powder. In the mean time, so much heat is produced. that part of the water flies off in vapour. If the quan-

\* Kirwan's Miner. i. s.

Chap. III.

tion.

lime.

Book II. Division-I.

tity of lime slacked (as this process is termed) be great, the heat produced is sufficient to set fire to combustibles. In this manner, vessels loaded with lime have sometimes been burnt. When great quantities of lime are slacked in a dark place, not only heat but light also is emitted, as Mr Pelletier has observed \*. When slacked lime is weighed, it is found to be heavier than it was before. This additional weight is owing to the combination of part of the water with the lime; which water may be separated again by the application of a red heat; and by this process the lime becomes just what it was before being slacked +. Hence the reason of the heat evolved during the slacking of lime. Part of the water combines with the lime, and thus becomes solid; of course it parts with its caloric of fluidity, and probably also with a considerable quantity of caloric which exists in water even when in the state of ice: for when two parts of lime and one part of ice (each at 32°) are mixed, they combine rapidly, and their temperature is elevated to 212°. The elevation of temperature during the slacking of barytes and strontian is owing to the same cause. From the experiments of Mr Dalton it follows, that slacked lime, well dried in a moderate heat, is composed of 3 parts lime and 1 part water 1. This result does not differ much from the previous experiments of Lavoisier, who found that 1000 parts of lime, when slacked, were con-

Hydrate of lime.

\* Jour. de Phys. i. 22. ‡ Dr Black. ‡ Dalton's New System of Chemical Philosophy, i. 87. verted into 1287 parts\*. Slacked lime then may be Chap. III. considered as a bydrate of lime:

The smell perceived during the slacking of lime is owing to a part of that earth being elevated along with the vapour of the water; as evidently appears from this circumstance, that vegetable blues exposed to this vapour are converted into green:

Limestone and chalk, though they are capable of be. Difference ing converted into lime by burning, possess hardly any limestone of the properties of that active substance. They are tasteless, scarcely soluble in water, and do not perceptibly act on animal bodies. Now, to what are the new properties of lime owing? What alteration does it undergo in the fire?

It had been long known, that limestone loses a good deal of weight by being burned or calcined. It was natural to suppose, therefore, that something is separated from it during calcination. Accordingly, Van Helmont, Ludovicus, and Macquer, made experiments in succession, in order to discover what that something is; and they concluded from them that it is pure water, which the lime recovers again when exposed to the atmosphere. As the new properties of lime could hardly be ascribed to this loss, but to some other cause, Stahl's opinion, like all the other chemical theories of that wonderful man, was generally acceded to. He supposed that the new properties which lime acquired by calcination are owing entirely to the more minute division of its particles by the action of the fire. Boyle indeed had endeavoured to prove, that these properties are owing to

\* Lavoisier's Essays translated by Henry, p. 2303

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Vol: II:

between and lime.

## ALKALINE EARTHS

Book M. Division I. the fixation of fire in the lime; a theory which was embed braced by Newton and illustrated by Hales, and which Meyer new modelled, and explained with so much ingenuity and acuteness as to draw the attention of the most distinguished chemists. But while Meyer was thus employed in Germany, Dr Black of Edinburgh published in 1756 those celebrated experiments which form so brilliant an era in the history of chemistry.

Discovered byDrBlack.

He first ascertained, that the quantity of water separated from limestone during its calcination is not nearly equal to the weight which it lost. He concluded in consequence, that it must have lost something else than mere water. What this could be, he was at first at a loss to conceive; but recollecting that Dr Hales had proved that limestone; during its solution in acids, emits a great quantity of air; he conjectured that this might probably be what is lost during calcination. He calcined it accordingly, and applied a pneumatic apparatus to receive the product. He found his conjecture verified ; and that the air and the water which separated from the lime were together precisely equal to the loss of weight which it had sustained. Lime therefore owes its new properties to the loss of air; and limestone differs from lime merely in being combined with a certain quantity of air : for he found that, by restoring again the same quantity of air to lime, it was converted into limestone. This air, because it existed in lime in a fixed state, he called fixed air .. It was afterwards examined by Dr Priestley and other philosophers ; found to possess peculiar properties, and to be that species of gas now known by the name of carbonic acid gas. Lime then is the simple substance, and limestone is composed of carbonic acid and lime. Heat separates

the carbonic acid, and leaves the lime in a state of Chap. III. purity.

5. When lime is exposed to the open air, it gradually attracts moisture, and falls to powder; after which it soon becomes saturated with carbonic acid, and is again converted into carbonate of lime or unburnt limestone.

Water, at the common temperature of the atmosphere; dissolves less than 0.002 parts of its weight of lime \*. This solution is called *lime-water*. It is limped, has an acrid taste, and changes vegetable blue colours to green. One ounce troy of lime-water contains about one grain of lime. It is usually formed by throwing a quantity of lime in powder into pure water, allowing it to remain for some time in a close vessel, and then decanting the transparent solution from the undissolved lime. When lime-water is exposed to the air, a stony crust soon forms on its surface composed of carbonate of lime; when this crust is broken it falls to the bottom. and another succeeds it; and in this manner the whole of the lime is soon precipitated, by absorbing carbonic acid from the air.

6. Lime is not acted on by light, neither does it combine with oxygen.

7. Sulphur and phosphorus are the only simple com- Of combust bustibles with which it unites.

Sulphuret of lime may be formed by mixing its two component parts, reduced to a powder, and heating them in a crucible. They undergo a commencement

\* By my trials, lime water contains only one 758th of its weight of lime!

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Action of water.

tibles.

Sulphuret.

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## ALKALINE EARTHS

Book II. Division I. of fusion, and form an acrid reddish mass. When it is exposed to the air, or moistened with water, its colour becoming greenish-yellow, sulphureted hydrogen is formed, and the sulphuret is converted into a hydrogureted sulphuret, which exhales a very fetid odour of sulphureted hydrogen gas. This hydrogureted sulphuret may be formed also by boiling a mixture of lime and sulphur in about ten times its weight of water, or by sprinkling quicklime with sulphur, and then moistening it: the heat occasioned by the slacking of the lime is sufficient to form the combination. When this hydrogureted sulphuret is exposed to the air, it imbibes oxygen; which combines at first with the hydrogen, and afterwards with the sulphur, and converts the compound into sulphate of lime \*. When the solution of hydrogureted sulphuret of lime is kept in a close vessel, the sulphur gradually precipitates, and hydro-sulphuret of lime remains in solution.

The hydrogureted sulphuret of lime has the property of dissolving charcoal by the assistance of heat, and of retaining it in solution †. It acts very powerfully upon metals and metallic oxides.

Phosphuret. Phosphuret of lime may be formed by the following process: Put into the bottom of a glass tube, close at one end, one part of phosphorus; and, holding the tube horizontally, introduce five parts of lime in small lumps, so that they shall be about two inches above the phosphorus. Then place the tube horizontally among burning coals, so that the part of it which contains the lime may be made red hot, while the bottom of the tube con-

# Berthollet.

+ Fourcroy, ii. 174.

taining the phosphorus remains cold. When the lime becomes red hot, raise the tube, and draw it along the coals till that part of it which contains the phosphorus is exposed to a red heat. The phosphorus is immediately volatilized, and passing through the hot lime combines with it. During the combination the mass becomes of a glowing red heat, and a quantity of phosphureted hydrogen gas is emitted, which takes fire when it comes into the air. This curious process was contrived by Dr Pearson, to whom we are indebted for the discovery of the earthy phosphurets \*.

Phosphuret of lime has a deep brown colour, and is moulded into the shape of the tube. It has no smell, and falls to pieces in the air. It is insoluble in water; but it has the property of decomposing that liquid. Phosphureted hydrogen gas is emitted, which takes fire as soon as it comes to the surface of the water. Part of this gas combines with the phosphuret, and forms a kind of hydrogureted phosphuret. Hence it happens, that if phospuret of lime, after being kept for some time in water, be taken out and dried, it flames when muria-

and, the halfs, the has, white of each P 448

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\* Van Mons has proposed the following method; but it appears to me rather inferior to that which is described in the text :--Fill a small glass matrass two-thirds with carbonate of lime in powder. Put it into a sand bath, and expose it to a heat sufficient to drive off the carbonic acid. Towards the end of the process introduce gradually a third part of phosphorus, taking care to keep the lime in a red heat. The phosphorus melts, but is prevented from burning by the remains of carbonic acid, which it disengages from the lime. When the whole of the phosphorus is introduced, shut up the matrass with a stopper, provided with a valve to let gas escape, but permiting none to enter, and let the fire be immediately withdrawn. When quite cold, the phosphuret is to be put into dry phials with ground stoppers. See Jour, de Chim. iii. 75.

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Chap. III.

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## ALKALINE EARTHS.

Book II. Division I. tic acid is poured upon it, owing to the rapid emission of phosphureted hydrogen gas\*.

8. Lime does not combine with azote; but it unites, readily with muriatic acid, and forms muriate of lime.

Action of metals, 9. Lime facilitates the oxidizement of several of the metals, and it combines with several of the metallic oxides, and forms salts which have not hitherto been examined, if we except the compounds which it forms with the oxides of mercury and lead, which have been described by Berthollet.

And their exides. The red oxide of mercury, boiled with lime-water, is partly dissolved, and the solution yields by evaporation small transparent yellow crystals<sup>†</sup>. This compound has been called by some *mercuriate of lime*.

Lime water also dissolves the red oxide of lead, and (still better) litharge. This solution, evaporated in a retort, gives very small transparent crystals, forming prismatic colours, and not more soluble in water than lime. It is decomposed by all the alkaline sulphates, and by sulphureted hydrogen gas. The sulphuric and muriatic acids precipitate the lead. This compound blackens wool, the nails, the hair, white of eggs; but it does not affect the colour of silk, the skin, the yolk of egg, nor animal oil. It is the lead which is precipitated on these coloured substances in the state of oxide ; for all acids can dissolve it. The simple mixture of lime and oxide of lead blackens these substances a proof that the salt is easily formed ‡.

10. Lime does not combine with alkalies.

+ Berthollet, Ann. de Chim. i. 61

into dell'abilità relationatione

# Fourcrey, ii. 172.

; Berthollet, Ann. de Chim. i. 52.

11. One of the most important uses of lime is the for- Char. III. mation of mortar as a cement in building. Mortar is Mortar. composed of quicklime and sand reduced to a paste with water. When dry it becomes as hard as stone, and as durable; and adhering very strongly to the surfaces of the stones which it is employed to cement, the whole wall becomes in fact nothing else than one single stone. But this effect is produced very imperfectly unless the mortar be very well prepared.

The lime ought to be pure, completely free from carbonic acid, and in the state of a very fine powder: the sand should be free from clay, and partly in the state of fine sand, partly in that of gravel: the water should be pure ; and if previously saturated with lime, so much the better. The best proportions, according to the experiments of Dr Higgins, are three parts of fine sand, four parts of coarser sand, one part of quicklime recently slacked, and as little water as possible.

The stony consistence which mortar acquires is owing, partly to the absorption of carbonic acid, but principally to the combination of part of the water with the lime. This last circumstance is the reason, that if to common mortar one fourth part of lime, reduced to powder without being slacked, be added, the mortar when dry acquires much greater solidity than it otherwise would do. This was first proposed by Loriot\*: and a number of experiments were afterwards made by Morveau +. The proportions which this philosopher found to answer best are the following.

\* Jour. de Phys. iii. 231.

+ Ibid. vi. 311

## ALKALINE EARTHS.

Bock II. Division I.

Fine sand	0.3
Cement of well baked bricks	0.3
Slacked lime	0.2
Unslacked lime	0.2

1.0

The same advantages may be attained by using as little water as possible in slacking the lime. This was first pointed out by La Faye \*.

Higgins found that the addition of burnt bones improved mortar by giving it tenacity, and rendering it less apt to crack in drying; but they ought never to exceed one fourth of the lime employed.

When a little manganese is added to mortar, it acquires the important property of hardening under water; so that it may be employed in constructing those edifices which are constantly exposed to the action of Limestone is found not unfrequently combined water. with manganese; and in that case it becomes brown by calcination, instead of white. These native limestones are employed for making water mortar ; but good water mortar may be made by the following process, first proposed by Morveau: Mix together four parts of blue clay, six parts of black oxide of manganese, and 90 parts of limestone, all in powder. Calcine this mixture to expel the carbonic acid, mix it with 60 parts of sand, and form it into mortar with a sufficient quantity of water +.

The best mortar for resisting water is made by mixing with lime puzzollano, a volcanic sand brought from

\* Ibid. ix. 437.

+ Ann, de Chim. XXXVII. 259.

Italy. Morveau informs us that basaltes, which is very common in this country, may be substituted for puzzollano. It must be heated in a furnace, thrown while red-hot into water, and then passed through a sieve to reduce it to the proper size \*.

12. With respect to the composition of lime, nothing but Attempts conjecture was known till lately. From the theory of Beccher and Stahl, it was the general opinion of chemists that the earths and metallic oxides are of a similar nature. Neuman, in consequence of an experiment of Henkel, attempted to obtain a metal from chalk by heating it along with combustible substances ; but his experiments did not succeed +. The idea, however, was not abandoned ; for it was a favourite notion of Lavoisier that all the earths might be metallic oxides 1. About the year 1790, soon after the publication of Mr Lavoisier's book, Mr Tondi and Professor Ruprecht, both of Schemnitz, announced that they had obtained from barytes, by a strong heat, a metal which they called barbonium, of the colour of iron, and attracted by the magnet; from magnesia another, which they call austrum; a third from lime, also called austrum; and a fourth from allumina, which they denominated apulum. Their method of proceeding was to apply a violent heat to the earths, which were surrounded with charcoal in a Hessian crucible, and covered with calcined bones in powder. But these experiments were soon after repeated by Klaproth, Savoresi, and Tihauski; and these accurate chemists soon proved that the pretended metals

\* Ann. de Chim. XXXVII. 262. + Lewis, Neuman's Chemistry, p. 10. \$ Chemistry, p. 217. English Transl.

of the base of the cardin could

Chap. HL

to decompose lime.

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## ALKALINE EARTHS.

Book II. Division I. were all of them *phosphurets of iron*. The iron, by the violence of the heat, had been extracted from the crucible, and the phosphorus from the bones.

Still more lately Desormes and Morveau were led to infer from some experiments, that lime is composed of carbon, azote, and hydrogen, and magnesia of lime and azote \*. But the experiments of Dorracq have demonstrated that the results obtained by these chemists were owing to the impurity of the substances on which they operated ‡.

It is a mecallic perexide.

yel Mr Davy's discovery, that the fixed alkalies are me--tallic oxides, naturally led to the conclusion that the alkaline earths which resemble them so closely are simi--lar compounds. He accordingly exposed them in various states to the action of a galvanic battery, and found reason to conclude that his opinion of their nature was correct, though he found it much more difficult to decompose them and obtain their bases, than it had been to obtain potassium and sodium by similar processes. When acted upon under naphtha they were not distinctly decomposed. When fused with an excess of potash, and acted upon in that state, the results were rather more distinct, metallic substances appeared less fusible than potassium, which burnt the instant after they were formed, and produced a mixture of potash and the earth employed. When the earths were exposed to the action of electricity, mixed with the oxides of mercury, tin, lead, or silver, amalgams were produced, which exhibited properties indicating unequivocally, that they were mixtures of the base of the earth employed, and of the

\* Mem. del Instit. iii. 321. Ann. de Chim. xl. 171.

base of the metallicoxide mixed with it. But the quantity of amalgam obtained was too minute to admit of an accurate examination. While Mr Davy was engaged in these experiments, he received a letter from Professor Berzelius of Stockholm, informing him, that he and Dr Pontin had succeeded in decomposing barytes and lime, by negatively electrifying mercury in contact with them. Mr Davy immediately repeated this happy experiment, and succeeded completely in obtaining amalgams of the base of the earth employed.

To procure these amalgams in sufficient quantity for distilling off the mercury, and obtaining the base of the earth pure, Mr Davy combined his own previous method with that of Berzelius and Pontin. The earth was slightly moistened, mixed with one third of red oxide of mercury, and placed upon a plate of platinum connected with the positive end of the battery. A cavity was made in the earthy mixture, a globule of about 60 grains of mercury put into it, and this globule connected with the negative end of the battery by a platinum wire. The amalgams obtained in this way were distilled in glass tubes filled with the vapour of naphtha. The greater part of the mercury was easily driven off, but it was extremely difficult to separate the whole. The globule that remained behind was in all cases white like silver, solid, and extremely combustible. When exposed to the air it absorbed oxygen, and regenerated the earth from which it was obtained in a few minutes.

The metallic basis of lime Mr Davy has called cal- Calcium cium. He did not succeed in investigating its properties. It is white like silver, solid, and probably 4 or 8 times heavier than water. When heated in the open air it burns brilliantly, and quicklime is produced.

its base.

Chap. III.

Book II. Division I. Neither did Mr Davy succeed in his attempts to ascertain the proportion of the constituents of lime, though he was satisfied that calcium by absorbing oxygen is converted into lime \*.

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History.

ABOUT the beginning of the eighteenth century, a Roman canon exposed a white powder to sale at Rome as a cure for all diseases. This powder he called magnesia alba. He kept the manner of preparing it a profound secret; but in 1707 Valentini informed the public that it might be obtained by calcining the lixivium which remains after the preparation of nitre  $\ddagger$ ; and two years after, Slevogt discovered that it might be precipitated by potash from the mother ley  $\ddagger$  of nitre  $\S$ . This powder was generally supposed to be *lime* till Frederic Hoffman observed that it formed very different combi-

\* Davy's Electrochemical Researches on the decomposition of the earths, Un Phil. Trans. 1808.

+ De Magnesia Alba.

<sup>‡</sup> The mother ley is the liquid that remains after as much as possible of any salt has been obtained from it. Common salt, for instance, is obtained by evaporating sea-water. After as much salt has been extracted from a quantity of sea-water as will crystallize, there is still a portion of liquid remaining. This portion is the mother ley.

§ Diss. de Magnesia Alba.

### MAGNESIA.

nations with other bodies \*. But little was known Chap. III. concerning its nature, and it was even confounded with lime by most chemists, till Dr Black made his celebrated experiments on it in 1755. Margraff published a dissertation on it in 1759 +, and Bergman another in 1775, in which he collected the observations of these two philosophers, and which he enriched also with many additions of his own t. Butini of Geneva likewise published a valuable dissertation on it in 1779.

1. As magnesia has never yet been found native in a Preparastate of purity, it may be prepared in the following manner : Sulphate of magnesia, a salt composed of this earth and sulphuric acid exists in sea-water, and in many springs, particularly in some about Epsom; from which circumstance it was formerly called Epsom salt. This salt is to be dissolved in water, and half its weight of potash added. The magnesia is immediately precipitated, because potash has a stronger affinity for sulphuric acid. It is then to be washed with a sufficient quantity of water, and dried.

2. Magnesia thus obtained is a very soft white pow- properties. der, which has very little taste, and is totally destitute of smell. Its specific gravity is about 2.3 §. It converts delicate vegetable blues (paper, for instance, stained with the petals of the mallow) to green.

It is not melted by the strongest heat which it has been possible to apply; but Mr Darcet observed that, in a very high temperature, it became somewhat agglutinated. When formed into a cake with water, and

\* Obs. Phys. Chim. 1722, p. 105. and 177. + Opusc. ii. 20, 1 Ibid. i. 365. § Kirwan's Miner, i. 8.

Book II. Division I.

then exposed to a violent heat, the water is gradually driven off, and the magnesia contracts in its dimension; at the same time, as Mr Tingry informs us, it acquires the property of shining in the dark when rubbed upon a hot iron plate.

Action of water, 3. It is almost insoluble in water: for, according to Mr Kirwan, it requires 7900 times its weight of water at the temperature of  $60^{\circ}$  to dissolve it. It is capable, however, of combining with water in a solid state, like lime; for 100 parts of magnesia, thrown into water, and then dried, are increased in weight to 118 parts<sup>\*</sup>. Even when combined with carbonic acid (for which it has a strong affinity) it is capable of absorbing and retaining  $1\frac{1}{2}$  times its own weight of water without letting go a drop; but on exposure to the air<sub>5</sub> this water evaporates, though more slowly than it would from lime.

Magnesia has never yet been obtained in a crystallized form.

When exposed to the air, it attracts carbonic acid gas and water; but exceedingly slowly. Butini left a quantity of it for two years in a porcelain cup merely covered with paper; its weight was only increased  $\frac{1}{144}$ part.

Oxygen,

4. Magnesia does not combine with oxygen, nor is it altered by any of the compounds into which oxygen enters.

Simple combustibles, 5. The only one of the simple combustibles with which it can be united is sulphur. No person has hitherto succeeded in forming a phosphuret of magnesia.

# Bergman, i. 371.

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In this respect it differs from the other three alkaline Chap. HI. earths.

The sulphuret of magnesia may be formed by exposing a mixture of two parts of magnesia and one part of sulphur to a gentle heat in a crucible. The result is a yellow powder, slightly agglutinated, which emits very little sulphureted hydrogen gas when thrown into water. A moderate heat is sufficient to drive off the sulphur \*.

6. Magnesia does not combine with azote; but it Icombustible, unites with muriatic acid, and forms a compound called muriate of magnesia.

7. Magnesia has no action upon the metals; nor Metals, does it combine, as far as is known at present, with the metallic oxides, unless some intermediate substance be present.

8. Magnesia does not combine with the fixed alkalies, Alkalies. neither are its properties altered by these bodies : but it has a strong propensity to enter into triple compounds with ammonia.

9. Mr Kirwan has shown that there is but little affinity between strontian and magnesia. They do not melt when exposed to a strong heat, at least when the strontian exceeds or equals the magnesia +.

Equal parts of lime and magnesia, mixed together, and exposed by Lavoisier to a very violent heat, did not melt ; neither did they melt when Mr Kirwan placed them in the temperature of 150° Wedgewood. The following Table, drawn up by Mr Kirwan from his own

\* Fourcroy, ii. 16e.

+ Irisb Truns. v. 246, 247.

Book II. Division I.

experiments, shows the effect of heat on these two earths mixed together in different proportions.

1		the state of the	
-	Proportions.	Heat.	Effect.
and	80 Lime 20 Mag.	150° Wedg.	Went through the crucible.
	75 Lime 25 Mag.	160	Went through the crucible.
	66 Lime 33 Mag.		Went through the crucible.
	20 Lime 80 Mag.	165	Did not melt.
	33 Lime 66 Mag.	138	Did not melt.
	30 Lime 10 Mag.		Melted into a fine greenish yellow glass; but the crucible was corroded throughout.

Magnesia is used only in medicine. It is administered internally to remove acidity in the stomach.

Decomposition of magnesia. Magnesia, like lime, is a metallic peroxide. Mr Davy succeeded in decomposing it by the same process by which he decomposed the other alkaline earths. When moistened magnesia is exposed to the action of galvanism in contact with mercury, the earth is reduced, and its base amalgamated with mercury much more slowly than the other alkaline earths; owing probably to its insolubility in water. The process succeeds much more rapidly when moistened sulphate of magnesia is substituted for the pure earth. To the base of magne-

### BARYTES: ANIA

sia thus obtained, Mr Davy has given the name of mag. Chap. Ill. nium. It is a white solid metal, having the appearance of silver ; sinks rapidly in water; and of course is considerably heavier than that liquid. When the amalgam of magnium is distilled in a glass tube filled with the vapour of naphtha, the metal appears to act upon the glass before the whole of the mercury is separated from it. Of course it is difficult to obtain it in a state of purity. When exposed to the air it rapidly absorbs oxygen, and is converted into magnesia. It decomposes water, separating the hydrogen, and combining with the oxygen; but not nearly so rapidly as the other metals obtained from the alkaline earths; owing doubtless to the insolubility of the magnesia in water-But when the water is acidulated with sulphuric acid, the decomposition of water and the formation of magnesia goes on with great rapidity \* Hard His many north

### SECT. III.

### OF BARYTES.

BARYTES was discovered by Scheele in 1774; and the History first account of its properties published by him in his Dissertation on Manganese 7. There is a very heavy minetal, most frequently of a flesh colour, of a foliated

\* Davy's Electrochemical Researches on the Decomposition of the Earths, Sc. Phil. Trans. 1808. † Scheele, i. 61 and 78: French Tsanslatiou. Vol. II. E

Book II. Division I. texture and brittle, very common in Britain and most other countries, especially in copper mines. 1 It was known by the name of ponderous spar, and was supposed to be a compound of sulphuric acid and lime. Gahn analysed this mineral in 1775, and discovered that it is composed of sulphuric acid and the new earth discovered by Scheele \*. Scheele published an account of the method of obtaining this earth from ponderous spar ta The experiments of these chemists were confirmed by Bergman 1, who gave the earth the name of terra ponderosa. Morveau gave it the name of barote, and Kirwan of Barytes \$ ; which last was approved of by Bergman ||, and is now universally adopted. Different processes for obtaining barytes were published by Scheele, Bergman, Wiegleb, and Afswelius; but little addition was made to the properties ascertained by the original discoverer, till Dr Hope published his experiments in 1793 ¶. In 1797, our knowledge of its nature was still farther extended by the experiments of Pelletier, Fourcroy, and Vauquelin \*\*.

Preparation. 1. Barytes may be obtained from ponderous spar, or sulphate of barytes, as it is now called, by the following process, for which we are indebted to Scheele and Vauquelin. Reduce the mineral to a fine powder; mix it with the eighth part of its weight of charcoal powder, and keep it for some hours red hot in a crucible, and it will be converted into sulphuret of barytes. Dissolve. the sulphuret in water, and pour nitric acid into the

- \* Bergman's Notes on Scheffer, § 167.
- + Crell's Annals, iii. 3. Eng. Trans.
  - § From Bapus, heavy.

‡ Opusc. iii. 291. || Opusc. iv. 261.

101. 11.

Fdin. Trans. iv. 36. ... \*\* Ann. de Chim. xxi. 113 and 276.

#### LIALINE EAR BARYTES.

solution, and the sulphur will be precipitated. The solution, which consists of nitric acid combined with barytes, is to be filtered and evaporated slowly till it crys-Put the crystals into a crucible, and expose tallizes. them gradually to a strong heat; the nitric acid is driven off, and the barytes remains in a state of purity \*.

Another method, attended with less expence, was pointed out long ago by Dr Hope, and afterwards improved by Pelletier. The method is this : Decompose the sulphate of barytes by heating it strongly along with charcoal powder. The product is to be treated with water to dissolve every thing that is soluble; and the liquid, being filtered, is to be mixed with a solution of carbonate of soda. A white powder falls. Wash this powder, make it up into balls with charcoal, and heat it strongly in a crucible. When these balls are treated with boiling water, a portion of barytes is dissolved, which crystallizes as the water cools.

2. Barytes obtained by the first method is a greyishwhite, porous body, which may be very easily reduced to powder. It has a harsh and more caustic taste than lime; and when taken into the stomach proves a most violent poison. It has no perceptible smell. It tinges vegetable blues green, and decomposes animal bodies like the fixed alkalies, though not with such energy.

Its specific gravity, according to Fourcroy +, is 4; but according to Hassenfratz only 2.374 ‡. But there is reason to conclude, from the method employed by this

\* When thus prepared, it always contains about 0.08 of carbonate of barytes, and sometimes much more. t Ann. de Chim. XXVIII. II.

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+ Fourcroy, ii. 189.

Properties.

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Chap. III.

Book II. Division I. philosopher, that the specific gravities which he assigns are all too low.

are all too low. When heated it becomes harder, and acquires internally a bluish-green shade. When exposed to the blowpipe on a piece of charcoal, it fuses, bubbles up, and runs into globules, which quickly penetrate the charcoal \*. This is probably in consequence of containing water, for Lavoisier found barytes not affected by the strongest heat which he could produce.

When exposed to the air, it immediately attracts moisture; in consequence of which it swells, heat is evolved, and the barytes falls to a white powder, just as happens to quicklime when water is sprinkled on it+. After the barytes is thus *slacked*, it gradually attracts carbonic acid, and loses its acrid properties, its weight being increased 0.22 <sup>‡</sup>. It cannot therefore be kept pure except in close vessel's.

Action of water. 3. When a little water is poured upon barytes, it is slacked like quicklime, but more rapidly, and with the evolution of more heat. The mass becomes white, and swells considerably. If the quantity of water be sufficient to dilute it completely, the barytes crystallizes in cooling, and assumes the appearance of a stone composed of needle. form crystals; but when exposed to the air, it gradually attracts carbonic acid, and falls to powder §.

Water is capable of dissolving 0.05 parts of its weight of barytes. This solution, which is known by the name of barytes water, is limpid and colourless, has

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- \* Fourcroy and Vauquelin, Ann. de Chim. Ixi. 276.
- + Id. ibid. ii. 59: f Mem. de l' Instit. it. 55

<sup>§</sup> Fourcroy, ü. 193.

# BARYTES.

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Chap. III.

an acrid taste, and converts vegetable blues first to a green, and then destroys them. When exposed to the air, its surface is soon covered with a stony crust, consisting of the barytes combined with carbonic acid.

Boiling water dissolves more than half its weight of barytes. As the solution cools, the barytes is deposited in crystals; the shape of which varies according to the rapidity with which they have been formed. When most regular, they are flat hexagonal prisms, having two broad sides, with two intervening narrow ones, and terminated at each end by a four-sided pyramid, which in some instances constitutes the larger part of the crystal. When formed slowly they are distinct and large; but when the water is saturated with barytes, they are deposited rapidly, and are generally more slender and delicate. Then, too, they are attached to one another in such a manner as to assume a beautiful foliaccous appearance, not unlike the leaf of a fern \*.

These crystals are transparent and colourless, and appear to be composed of about 53 parts of water and 47 of barytes. When exposed to the heat of boiling water, they undergo the watery fusion; that is to say, the water which they contain becomes sufficient to keep the barytes in solution. A stronger heat makes the water fly off. When exposed to the air, they attract carbonic acid, and crumble into dust. They are soluble in  $17\frac{1}{2}$  parts of water at the temperature of  $60^\circ$ ; but boiling water dissolves any quantity whatever: the reason of which is evident; at that temperature their own water of crystallization is sufficient to keep them in solution  $\ddagger$ .

\* Hope, E din. Trans. iv. 36.

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+ Ibid.

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Book II, Division I. Action of oxygen, Of the simple combustibles. 4. Barytes undergoes no change from light; neither is it capable, as far as is known, of combining with oxygen,

5. None of the simple combustibles combine with it, except sulphur and phosphorus.

Sulphuret of barytes may be formed by mixing its two ingredients together and heating them in a crucible. The mixture melts at a red heat, and when cold forms a mass of a reddish-yellow colour, without any smell, which is sulphuret of barytes. This sulphuret decomposes water with great rapidity ; sulphureted hydrogen is formed, which, combining with the sulphuret, converts it into a hydrogureted sulphuret. This change takes place whenever the sulphuret is moistened with water, or even exposed to the atmosphere. When boiling water is poured upon sulphuret of barytes, a great quantity of sulphureted hydrogen is formed almost instantaneously, which combines with the water, and occasions the solution of the sulphuret. When the solution cools, a great number of brilliant white crystals are deposited, sometimes in the form of needles, sometimes in six-sided prisms, and sometimes in hexagonal plates. These crystals are composed of sulphureted hydrogen and barytes, and have been called by Berthollet, to whom we are indebted for the first accurate account of them, hydrosulphuret of barytes. The liquid which has deposited the hydrosulphuret is of a yellow colour, and holds in solution a bydrogureted sulphuret of barytes \*.

Phosphuret.

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Phosphuret of barytes may be formed by putting phosphorus and barytes into a glass tube close at one

\* Berthollet, Ann. de Chim. xxv. 233.

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### BARYTES. A

end, and heating the tube upon burning coals, as in making phosphuret of lime. The combination takes place very rapidly. This phosphuret is of a dark brown colour, very brilliant, and very fusible. When moistened, it exhales the odour of phosphureted hydrogen gas. When thrown into water, it is gradually decomposed, phosphureted hydrogen gas is emitted, which takes fire when it comes to the surface of the water, and the phosphorus is gradually converted into phosphoric acid\*.

6. Barytes is not acted on by azote; but it combines readily with muriatic acid, and forms a compound called *muriate of barytes*.

7. Barytes has no action on metals; but it is capable of combining with several of the metallic oxides, and forming with them compounds which have not hitherto been much examined. For instance, if it be poured into a solution of silver or lead in nitric acid, it precipitates the first brown, and the second white; but if an excess of barytes water be added, the precipitates are redissolved  $\dagger$ .

8. Barytes does not combine with the alkalies.

9. We are indebted to Bucholz for a set of experiments on the action of barytes on the other earthy bodies. Lime does not seem to unite with it. When equal quantities of the two earths are heated in a crucible, a mass is obtained, having some cohesion, but soluble in water ‡. The phenomena were nearly the

\* Fourcroy, ii. 191.

+ Fourcroy and Vauquelin, Mem. de l'Instit. ii. 61. 1 . . .

# Bucholz's Beitrage, iii. 59. He seems not to have used pure lime, but a submuriate. Action of incombustibles.

Action of metals and their oxides.

Of alkalies.

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Concitu-

Book II. Division 1.

Constitupnts of barytes.

same when barytes and magnesia were heated together, When the resulting mass was treated with water, the barytes dissolved, but took up more of the magnesia \*, 10. Barytes, like the other alkaline earths, has been demonstrated by Mr Davy to be a metallic peroxide. To the metal which constitutes its base, the name of barl; um has been given. Mr Davy succeeded in obtaining this metal, by placing a mixture of barytes and oxide of mercury in contact with a globule of mercury, and exposing it to the action of a galvanic battery. The barytes was decomposed, and its base amalgamated with the mercury. The amalgam was then heated in a glass tube filled with the vapour of naphtha, to drive off the mercury. Barium, thus obtained, is a solid metal of the colour of silver, it melis at a temperature below redness, and is not volatilized by a heat capable of melting plate glass, but at that temperature it acts violently upon the glass; probably decomposing the alkali of the glass, and converting it into a protoxide. When exposed to the air it rapidly tarnishes, absorbs oxygen, and is converted into barytes: It sinks rapidly in water, and seems to be at least four or five times heavier than that liquid? It decomposes water with great rapidity ; hydrogen is emitted, and it is converted into barytes. When strongly pressed it becomes flat, and hence appears to be both ductile and malleable. The proportion of oxygen necessary to convert barium into barytes; has not been ascertained +.

† Davy's Electrochemical Researches on the Decomposition of the Bartle, Poil, Trans. 1808. of groutiers. Klamonis making it also in 1703, and

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e described, ello this court Isr Hope gave the same

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sed still unpublished. IV. SECT. 1V. Sitwan also discovered the most anaresting peculiarities of this new earth in I .... ALTRONTROFTO Crell. though his discrigition on it, which was read to the

drew the same come

About the year 1787 a mineral was brought to Edinburgh, by a dealer in fossils, from the lead mine of Strontian, in Argyleshire, where it is found imbeded in the ore, mixed with several other substances. It is sometimes transparent and colourless, but generally has a tinge of yellow or green. Its hardness is 5. Its specific gravity varies from 3'4 to 3'726. Its texture is generally fibrous; and sometimes it is found crystallized in slender prismatic columns of various lengths \*.

This mineral was generally considered as a carbonate of barytes; but Dr Crawford having observed some differences between its solution in muriatic acid and that of barytes, mentioned in his treatise on muriate of barytes, published in 1790, that it probably contained a new earth, and sent a specimen to Mr Kirwan, that he might examine its properties. Dr Hope made a set of experiments on it in 1791, which were read to the Royal Society of Edinburgh in 1792, and published in the Transactions about the beginning of 1794. These experiments demonstrate, that the mineral is a compound of carbonic acid, and a peculiar earth, whose properties

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History.

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Chap. III.

Book II. Division I. ~

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are described. To this earth Dr Hope gave the name of strontites. Klaproth analysed it also in 1793, and drew the same conclusions as Dr Hope, though he was ignorant of the experiments of the latter, which remained still unpublished. Klaproth's experiments were published in Crell's Annals for 1793\* and 1794+. Kirwan also discovered the most interesting peculiarities of this new earth in 1793, as appears by his letter to Crell, though his dissertation on it, which was read to the Irish Academy in 1794, was not published till 1795. The experiments of these philosophers were repeated and confirmed in 1797 by Pelletier, Fourcroy, and Vauquelin ‡, and several of the properties of the earth still farther investigated. To the earth thus detected Klaproth gave the name of strontian, from the place where it was first found ; and this name is now generally adopted. scierally fibrous; and fomet

Strontian is found abundantly in different places of the world, and always combined with carbonic acid or sulphuric acid. of parvies ; but Dr Clawford having

Preparation.

1. The carbonic acid may be expelled from the carbonate, and the strontian obtained pure, by mixing the mineral with charcoal powder, and exposing it to a heat of 140° Wedgewood §; or by dissolving the mineral in nitric acid, evaporating the solution till it crystallizes. and exposing the crystals in a crucible to a red heat till the nitric acid is driven off. Strontian may be obtained

Transcions about the legitaring of 3 764. X3 SPORT periments demonstrate, that the mineral is a compound \* Vol. ii. 189. † Vol. i. 99. See also Klaproth's Beitrage, i. 260. and Jeur. de Min.

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\$ Ann. de Chim. xxi. 113. and 276. Jour. de Min. An. vi. 3.

& Kirwan.

### STRONTIAN.

from the sulphate by following exactly the process described in the last Section for obtaining barytes.

2. Strontian, thus obtained, is in porous masses, of a greyish white colour ; its taste is acrid and alkaline ; and it converts vegetable blues to green. Its specific gravity, according to Hassenfratz, is 1.647 \*. It does not act so strongly on animal bodies as barytes, nor is it poisonous +.

It does not melt when heated, like barytes; but be- "2120 30 fore the blowpipe it is penetrated with light, and surrounded with a flame so white and brilliant that the eye can scarcely behold it 1.

3. When water is sprinkled on strontian it is slacked. becomes hot, and falls to powder exactly like barytes; but it is not so soluble in water as that earth. One hundred and sixty-two parts of water, at the temperature of 60°, dissolve nearly one part of strontian. The solution, known by the name of strontian water, is clear and transparent, and converts vegetable blues to a green. Hot water dissolves it in much larger quantities; and as it cools, the strontian is deposited in colourless transparent crystals. These are in the form of thin quadrangular plates, generally parallelograms, the largest of which seldom exceeds one-fourth of an inch in length. Sometimes their edges are plain, but they oftener consist of two facets, meeting together, and forming an angle like the roof of a house. These crystals generally adhere to each other in such a manner as to form a thin plate of an inch or more in length and half an inch

+ Pelletier, Ibid. xxi. 120. · Ann. de Chim. XXVIII. II. ‡ Fourcroy, ii. 227. \* V sugada, Jow de Min. An. Chap. III.

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Rook IL Division I. in breadth. Sometimes they assume a cubic form. They contain about 68 parts in 100 of water. They are soluble in 51.4 parts of water at the temperature of 60°. Boiling water dissolves nearly half its weight of them. When exposed to the air, they lose their water, attract carbonic acid, and fall into powder\*. Their specific gravity is 1.46 <sup>†</sup>. 4. Strontian is not acted on by light; neither does it

Of oxygen,

Of combustibles.

Sulphuret.

Phosphutct.

Action of incombustibles, metals, and alcombine with oxygen. 6. Sulphur and phosphorus are the only simple com-

bustibles with which it unites ‡. The sulphuret of strontian may be made by fusing the two ingredients in a crucible. It is soluble in water by means of sulphureted hydrogen, which is evolved. When the solution is evaporated, bydrosulphuret of strontian is obtained in crystals, and bydrogureted sulphuret remains in solution. These three compounds resemble almost exactly the sulphuret, bydrosulphuret, and hydrogureted sulphuret of barytes; and do net therefore require a particular description. The same remark applies to the phosphuret of strontian, which may be prepared by the same process as the phosphuret of barytes §.

6. Strontian does not combine with azote; but it unites readily with muriatic acid, and forms the substance called muriate of strontian.
7. Strontian has no action upon metals; but it com-

7. Strontian has no action upon metals; but it combines with several of their oxides, and forms compounds which have not hitherto been examined.

\* Hope, Edin. Truns. iv. 44. † Hass n'ratz, Ann. de Chim. XXVIII. 11. \* Vauguelin, Jour. de Min. An. vi. 17. § Ibid.

S. It does not combine with alkalies nor with barytes. No precipitation takes place when barytes and strontian water are mixed together \*.

9. Strontian has the property of tinging flame of a beautiful red, or rather purple colour; a property discovered by Dr Ash in 1787. The experiment may be made by putting a little of the salt composed of nitric acid and strontian into the wick of a lighted candle +; or by setting fire to alcohol, holding muriate of strontian in solution. In both cases the flame is of a lively purple. In this respect it differs from barytes, which when tried in the same way is found to communicate a bluish yellow tinge to the flame 1.

Barytes and strontian resemble each other in their properties as closely as potash and soda : hence, like these two alkalies, they were for some time confounded. It is in their combination with acids that the most striking differences between these two earths are to be observed.

Strontian, like the other alkaline earths, has been de- Composicomposed by Mr Davy, and by a similar process. The metallie bases of it has been called strontium. It is white, solid, much heavier than water, and bears a close, resemblance to barium in its properties. When exposed to the air, or when thrown into water, it rapidly absorbs oxygen, and is converted into strontian §.

SECT I.

AKIMULA TO

\* Morveau, Ann. de Chim. XXXI. 251.

A Vauquelin, Jour. de Min. An. vi. 10. . doithy the set DUTE.

1 Pelletier, Ann. de Chim. xxi. 137. b ai mont vi bezolitate bas

& Davy's Electrochemical Researches into the Decomposition of the Earthey Cr. Phil. Trans. 1808. to bios anutation to becommonie is tails

Chap. III.

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History.

### EARTHS PROPER. 3. It does not combine fei a ala dies nor with bary-

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Book II. Division I

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#### ointin 1 OF EARTHS PROPER. THE a lighter condict;

THE Earths proper are distinguished from the alkaline by neither producing any change on vegetable blues nor neutralizing acids. Indeed some of them scarcely unite to these bodies. The earths proper are five in number; namely, ed. wit is in their constantion wat

or breather lies to slook . holding muriate of strongian in solution. In both cases, a flamais of a lively purple. listhingespeet is differs from burytes, which when the

> ALUMINA, Statistic gasting YTTRIA, GLUCINA, die offe offentie ZIRCONIA, WE (I MA yd heogano

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We shall examine their properties in the following Sections. resemblance to Eirram in its propertie

### antitatie dial forter tax et bas, norte a SECT. I.

### OF ALUMINA.

History.

ALUM is a salt which was well known to the ancients. and employed by them in dyeing, but they were ignorant of its component parts. The alchymists discovered that it is composed of sulphuric acid and an earth; but

### ALUMINA. HI AL

the nature of this earth was long unknown. Stahl and Chap. IV. Neuman supposed it to be lime; but in 1727 Geoffroy junior proved this to be a mistake, and demonstrated, that the earth of alum constitutes a part of clay \*. In 1754, Margraff showed that the basis of alum is an earth of a peculiar nature, different from every other ; an earth which is an essential ingredient in clays, and gives them their peculiar properties +. Hence this earth was called argil; but Morveau afterwards gave it the name of alumina, because it is obtained in the state of greatest purity from alam. The properties of alumina were still farther examined by Macquer in 1758 and 1762 1, by Bergman in 1767 and 1771 ||, and by Scheele in 1776 6; not to mention several other chemists who have contributed to the complete investigation of this earth. A very ingenious treatise on it was published by Saussure junior in 1801 ¶.

1. Alumina may be obtained by the following process: Dissolve alum in water, and add to the solution ammonia as long as any precipitate is formed. Decant off the fluid part, and wash the precipitate in a large quantity of water, and then allow it to dry. The substance thus obtained is *alumina*; not however in a state of absolute purity, for it still retains a portion of the sulphuric acid with which it was combined in the alum. But it may be rendered tolerably pure by dissolving the newly precipitated earth in muriatic acid, evaporating the solution till a drop of it in cooling deposits small

Preparation.

Propertie.

LY OF ARTINTE

Book II. Division I. crystals, setting it by to crystallize, separating the crystals, concentrating the liquid a second time, and separating the crystals which are again deposited. By this process most of the alum which the earth retained will be separated in crystals. If the liquid be now mixed with ammonia as long as any precipitate appears, this precipitate, washed and dried, will be *alumina* nearly, pure \*.

The earth thus obtained assumes two very different appearances according to the way in which the precipitation has been conducted. If the earthy salt be dissolved in as little water as possible, the alumina has the appearance of a white earth, light, friable, very spongy, and attaching itself strongly to the tongue. In this state Saussure distinguishes it by the name of spongy alumina.

But if the salt has been dissolved in a great quantity of water, the alumina is obtained in a brittle transparent yellow-coloured mass, splitting in pieces like roll sulphur when held in the hand. Its fracture is smooth and conchoidal; it does not adhere to the tongue, and has not the common appearance of an earthy body. In this state Saussure gives it the name of gelatinous alumina +.

Properties.

2. Alumina has little taste: when pure, it has no smell; but if it contains oxide of iron, which it often does, it emits a peculiar smell when breathed upon, known by the name of *earthy smell*  $\ddagger$ . This smell is very perceptible in common clays. The specific gravity of alumina is 2.00 ||.

\* Accum's Chemistry, ii. 198. ‡ Saussure, Jour. de Phys. lii. 287. Kirwan's Miner. i. \$

3. When heat is applied to alumina it gradually loses weight, in consequence of the evaporation of a quantity of water with which, in its usual state, it is combined; at the same time its bulk is considerably diminished. The spongy alumina parts with its moisture very readily, but the gelatinous retains it very strongly. Spongy alumina, when exposed to a red heat, loses 0.58 parts of its weight; gelatinous, only 0.43: Spongy alumina loses no more than 0.58 when exposed to a heat of 130° Wedgewood; gelatinous in the same temperature loses but 0.4825. Yet Saussure has shown that both species, after being dried in the temperature of 60°, contain equal proportions of water \*. have been ext

Alumina undergoes a diminution of bulk proportional to the heat to which it is exposed. This contraction seems owing, in low temperatures, to the loss of moisture : but in high temperatures it must be owing to a more intimate combination of the earthy particles with each other; for it loses no perceptible weight in any temperature, however high, after being exposed to a heat of 130° Wedgewood +.

Mr Wedgewood took advantage of this property of Wedges alumina, and by means of it constructed an instrument for measuring high degrees of heat. It consists of pieces of clay of a determinate size, and an apparatus for measuring their bulk with accuracy : One of these pieces is put into the fire, and the temperature is estimated by the contraction of the piece 1. The contraction of the clay-pieces is measured by means of two

Action of

\* Jour. de Pbys. lii. 287.

‡ See a particular description of this thermometer in Pbil. Trans. lxii. and laiv. 10.00

Vol. II.

Chap. IV. Contracted by heat.

+ Ibid.

word's pyrometer

### EARTHS PROPER.

Book II. Division I. brass rules fixed upon a plate. The distance between which at one extremity is 0.5 inch, and at the other extremity 0.3 inch, and the rules are exactly 24.0 inches in length, and divided into 240 equal parts, called degrees. These degrees commence at the widest end of the scale: The first of them indicates a red heat, or 947° Fahrenheit. The clay-pieces are small cylinders, baked in a red heat, and made so as to fit 1° of the scale. They are not composed of pure alumina, but of a fine white clay.

Unfortunately the contraction of these pieces is not always proportional to the degree of heat to which they have been exposed, nor do they correspond exactly with each other. The instrument, notwithstanding, is certainly valuable, and has contributed considerably towards the extension of our knowledge.

Alumina, when exposed to a very violent heat, produced by directing a stream of oxygen gas upon burning charcoal, undergoes a commencement of fusion, and is converted into a white enamel, semitransparent, and excessively hard \*. If we put any confidence in the calculation of Saussure, the temperature necessary for producing this effect is as high as 1575° Wedgewood t.

Action of water.

4. Alumina is scarcely soluble in water, but may be diffused through that liquid with great facility. Its affinity for water, however, is very considerable. In its usual state it is combined with more than its own weight of water, and we have seen with what obstinacy

> \* Morveau, Jour. de l'Ecole Polytechnique, 1. ni. 299. + Jour- de Phys. 3794. Fel. 11.

wiel birs

### ALUMINA

it retains it. Even this combination of alumina and water is capable, in its usual state of drynes, of absorbing 21 times its weight of water, without suffering any to drop out. It retains this water more obstinately than any of the earths hitherto described. In a freezing cold it contracts more, and parts with more of its water, than any other earth ; a circumstance which is of some importance in agriculture \*. Device and at acalan , an

Alumina has no effect upon vegetable blues. It cannot be crystallized artificially; but it is found native in beautiful transparent crystals, exceedingly hard, and having a specific gravity of 4. It is distinguished in this state by the name of sappbyr. IO. Bary

5. Alumina, as far as is known at present, is not affected by light, neither does it combine with oxygen.

6. None of the simple combustibles are capable of uniting with it. Charcoal indeed combines with it, and forms a black compound t, which is frequently found native:

7. It is not acted on by azote; but muriatic acid Incombusdissolves it, and forms with it an uncrystallizable compound, called muriate of alumina.

8. It does not combine with metals; but it has a strong affinity for metallic oxides; especially for those oxides which contain a maximum of oxygen. Some of these compounds are found native. Thus, the combination of alumina and red oxide of iron often occurs in the form of a yellow powder, which is employed as a paint, and distinguished by the name of ochre.

9. There is a strong affinity between the fixed alkalies Alkalies

\* Kirwan's Miner. i. 9.

+ Nicholson's Journal, ii. 101. F 2

Action of oxygen,

Birrees and

Combustibles.

tibles,

Metals:

Chap. IV.

### EARTHS PROPER.

Book II. Division I. and alumina. When heated together, they combine and form a loose mass without any transparency. Liquid fixed alkali dissolves alumina by the assistance of heat, and retains it in solution. The alumina is precipitated again unaltered, by dropping an acid into the solution. This is the method employed by chemists to procure alumina in a state of complete purity; for alumina, unless it be dissolved in alkali, almost always retains a little oxide of iron and some acid, which disguise its properties. Liquid ammonia is also capable of dissolving a very minute proportion of newly precipitated alumina.

Barytes and strontian,

OXYEST,

10. Barytes and strontian also combine with alumina, both when heated with it in a crucible, and when boiled with it in water. The result, in the first case, is a greenish or bluish-coloured mass, cohering but imperfectly: in the second, two compounds are formed; the first, containing an excess of alumina, remains in the state of an insoluble powder; the other, containing an excess of barytes or strontian, is held in solution by the water \*.

### Lime,

Metels

Alumina has a strong affinity for lime, and readily enters with it into fusion. The effect of heat on various mixtures of lime and alumina will appear from the following TABLE +.

\* Vauquelin, Ann. de. Chim. xxix. 270. See also Bucholz's Beitrage, iii 58. † Kirwan, i. 65.

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· Frent's Miner i a

9. There is a strong afficity between the fixed alkalies Alkalies.

t Michologie Jureal, il. 191

Thue the combi-

#### ALUMINA.

Proportions.	Hcat.	Sull' Effect.
75 Lime 25 Alumina	150° Wedg.	Not melted.
66 Lime 33 Alumina	A porcelain	Remained a powder.
33 Lime 66 Alumina	Porous poro	Melted E
25 Lime 75 Alumina	*	Melted.
20 Lime 80 Alumina-	*	Melted.

Magnesia and alumina have no action whatever on Magnesia. each other, even when exposed to a heat of 150° Wedgewood t.

From the experiments of Achard, it appears, that no mixture of lime, magnesia, and alumina, in which the lime predominates, is vitrifiable, except they be nearly in the proportions of three parts lime, two magnesia, one alumina; that no mixture in which magnesia predominates will melt in a heat below 166° : that mixtures in which the alumina exceeds are generally fusible, as will appear from the following TABLE T.

\* These three experiments were made by Ehrman : The heat, was produced by directing a stream of oxygen gas on burning charcoal, and is the most intense which it has been kitherto possible to produce of a Kirwan's Miner, i. 57; Junii Dan it bid. P. 72. diorgel -

tween alout <del>and the sairs which established with</del> makes with

shis protended metal was only phosphuret of iron. MI Davy's discovery, that the alkalies and alkaline carthen

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Chap. IV

EARTHS PROPER.

ok II. sion I.	3 Alumina 2 Lime 1 Magnesia	A porcelain.
wder.	3 Alumina 1 Lime 2 Magnesia	A porcelain.
sing and roganics roganics	3 Alumina 1 Lime 3 Magnesia	Porous porcelain.
	3 Alumina 2 Lime 3 Magnesia	Porous porcelain.
tever tever dan tever on trong Wednes	3 Alumina 2 Lime 2 Magnesia	Porcelain.

None of the earths is of more importance to mankind than alumina; it forms the basis of china and stoneware of all kinds, and of the crucibles and pots employed in all those manufactures which require a strong heat. It is absolutely necessary to the dyer and calicoprinter, and is employed too with the greatest advantage by the fuller and cleaner of cloth.

Composition of alumina. That alumina might be a metallic oxide was supported many years ago by Baron, from the resemblance between alum and the salts which sulphuric acid makes with metallic oxides. Tondi and Ruprecht announced about 1790, that they had decomposed it, and gave to the metal which they obtained from it the name of *apulum*. But Klaproth, Savoresi, and Tihauski demonstrated, that this pretended metal was only phosphuret of iron. Mr Davy's discovery, that the alkalies and alkaline earths

Boo

are metallic oxides, naturally led to the notion that the earths proper are of the same nature. Accordingly he made a number of experiments on the subject, and has rendered the opinion probable, though he has not been able to demonstrate it in so satisfactory a manner as could have been wished. When a mixture of potash and alumina, in a state of fusion in a platinum crucible, in contact with the positive end of a galvanic battery, is touched by a platinum wire from the negative extremity, a bright combustion takes place, and metallic globules separate and burn brilliantly on the surface. The platinum, when taken out and freed from the alkali, is surrounded with metallic scales, which burn spontaneously when exposed to the air, and which decompose water with great rapidity, producing potash and an earthy matter, which was probably alumina. Potassium, amalgamated with about one third of mercury, was electrified under naphtha in contact with alumina slightly moistened. After an hour the potassium was made to decompose water, and the alkali formed neutralized. A cloudiness appeared, indicating the presence of an earthy substance. Such were the most sucessful experiments that Mr Davy was able to make in his attempts to decompose alumina and reduce it to the state of a metal. Supposing that a metallic base can be successfully extracted from it, he proposes to give that metal the name of alumium \*. Klaush about the same

\* Davy's Electrochemical Researches on the decomposition of the earths, Sc. Phil. Trans. 1808.

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Chap. IV.

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Book II. Division 1.

History.

are metallic oxides, naturally led to the notion that the earths proper are of the same nature. Accordingly he made a number of experiments on the subject, and has rendered the opinion probable, though he has not been able to demonstrate it igth sTDES av a manner as could have been wished. When a mixture of potash and aluteina, in a state of fusioning a plating or unible, in contact with the positive end of a galvanic ballery, istouched by a platimum wire from the negative extremity, a bright SOME time before 1788, Captain Arhenius discovered, in the guarry of Ytterby in Sweden, a peculiar mineral different from all those described by mineralogists. Its colour is greenish black, and its fracture like that of glass. It is magnetic, and generally too hard to be scratched by a knife. It is opaque, except in small pieces, when it transmits some yellow rays. Its specific gravity is 4:237 \*. A description of it was published by Geyer in 1788 in Crell's, Annals, and by Rinman in his Miner's Lexicon. Professor Gadolin analysed this mineral in 1794, and found it to contain a new earth : but though his analysis was published in the Stockholm Transactions for 1794, and in Crell's Annals for 1796, it was some time before it drew the attention of chemical mineralogists. The conclusions of Gadolin were confirmed by Ekeberg in 1797, who gave to the new earth the name of yttria t. They were still farther confirmed and extended by Vauquelin in 1800 1, and likewise by Klaproth about the same time ||; and Eke-

\* Gadolin, Crell's Annals, 17,6, i. 313.-Vauquelin, Ann. de Chim. xxxvi. 146.-Klaproth's Beitrage, iii. 58.

\* They's Preparational Presenter in 181 (menterline o

+ Crell's Annals, 1799, ii. 63.

\$ Ann. de Chim. xxxvi. 143:

| Ibid, xxxvii. 86. and Beitrage, iii. 52.

### .....YTTRIA

berg has published a new dissertation on the subject in the Swedish Transactions for 1802 \*! b We may therefore consider the peculiar nature of yttria as sufficiently third of their weight, when heated to redne bidites

1. Hitherto yttria has been found only in the black mineral first analysed by Gadolin, and hence called Gadolinites in which it is combined with black oxide of iron and the earth called silica; and in yttrotantalite. which from the description of Ekeberg is a compound of tantalum and yttria. Both of these minerals occur only in the quarry of Ytterby. From the first, which is the most common, the earth may be procured by treating the mineral reduced to powder with a mixture of nitric and muriatic acids, till it is completely decomposed; then filtering the solution, previously evaporated nearly to dryness, and then diluting it with water. By this process the silica is left behind. The liquid which passes through the filter is to be evaporated to dryness, and the residue heated to redness for a considerable time in a close vessel, and then redissolved in water and filtered. What passes through the filter is colourless; when treated with ammonia, pure yttria falls. . 2. Yttria thus procured has the appearance of a fine Properties. white powder, and has neither taste nor smell. It is not melted by the application of heat. "It has no action on vegetable blues." It is much heavier than any of the other earths; its specific gravity, according to Ekeberg,

It is insoluble in water; yet it is capable of retaining a great proportion of that liquid, as is the case with

being no less than 4.842. think diw sister let of

\* Jour. de Chim. iii. 78.

Chap. IV.

Preparation.

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### EARTHS PROPER.

Book II. Division I.

Propara-

alumina. Klaproth ascertained, that 100 parts of yttria, precipitated from muriatic acid by ammonia, and dried in a low temperature, lose 31 parts, or almost a third of their weight, when heated to redness in a crucible. Now this loss consists of pure water alone.

It is not soluble in pure alkalies; but it dissolves readily in carbonate of ammonia, and in all the other alkaline carbonates. It combines with acids, and forms with them salts which have a sweet taste, and at the same time a certain degree of austerity. Some of these salts have a red colour. Yttria is the only earthy body known which has the property of forming coloured salts with acids.

azote; but it combines with muriatic acid, and forms a salt not capable of crystallizing. Its action on the metals and metallic oxides is unknown.

Composi-

No attempts have been made to decompose yttria, But from analogy there can be little doubt that, like the other earths, it is in reality a metallic peroxide. The experiments of Ekeberg, if correct, may be considered as a demonstration of the truth of this opinion. When he treated yttria with muriatic acid, oxymuriatic acid is said to have been evolved.

A greet proportion of that liquid, as is the one with

STATUS AND STATE WITH A HARTY

potash. Wash the presid

sulphuric acid. A dd to that solution sulph

and boil she liquid for some time of a white

in solution. Precipitate them by means of carliconate of .

nini se lostile mais

evaporate it to the proget. SECT. III.

many of these as possible have been obtained, pour in-OF GLUCINA.

THE beryl is a transparent stone, of a green colour, History. and a considerable degree of hardness, which is found crystallized in the mountains of Siberia, and in many other parts. Vauquelin analysed this mineral in 1796. at the request of Hauy, to determine whether it was formed of the same ingredients with the emerald, as Hauy had conjectured from mineralogical considerations. The result of the analysis was a confirmation of the suspicions of Hauy, and the discovery of a new earth, to which Vauquelin and his associates gave the name of glucina\*. The experiments of Vauquelin have been repeated by Klaproth † and other eminent chethe simple combustibles; but sulphureted hydroge stein

1. To obtain glucina pure, the beryl or the emerald, Preparareduced to powder, is to be fused with thrice its weight tion. of potash. The mass is to be diluted with water, dissolved in muriatic acid, and the solution evaporated to dryness. The residuum is to be mixed with a great quantity of water, and the whole thrown on a filter. The silica, which constitutes more than half the weight of the stone, remains behind; but the glucina and the other earths, being combined with muriatic acid, remain

Ann. de Chim. XXVi. X55.

+ Beitrage, ili. 215.

Chap. IV.

Irege La

### EARTHS PROPER.

Division I.

Book II. in solution. Precipitate them by means of carbonate of potash. Wash the precipitate, and then dissolve it in sulphuric acid. Add to the solution sulphate of potash; evaporate it to the proper consistency, and set it by to crystallize. Alum crystals gradually form. When as many of these as possible have been obtained, pour into the liquid carbonate of ammonia in excess, then filter, and boil the liquid for some time. A white powder gradually appears, which is glucina. It s at lyind and

Properties.

1.2. Glucina, thus obtained, is a soft light white powder, without either taste or smell ; which has the property of adhering strongly to the tongue. VIt has no action on vegetable colours. b It is altogether infusible by, heath neither does it harden or contract in its dimensions, as is the case with alumina. I Its specific gravity ations. The result of the analysis was a cost or ecsai

with is insoluble in water, but forms with a small quantity of that liquid a paste which has a certain degree of V name of glacina\*. The experiments of Vauque tilitarb

-93. It does not combine with oxygen nor with any of the simple combustibles; but sulphureted hydrogen dis-I solves it, and forms with it a hydrosulphuret, similar to other hydrosulphurets in its properties tog or boonbor

4. Azote has no action on it; but muriatic acid dissolves it, and forms with it a sweet-tasted salt, called dryness. The residuum is to be manipulg do statum

5. Glucina is soluble in the liquid fixed alkalies, in which it agrees with alumina. is It is insoluble in ammonia, but soluble in carbonate of ammonia, in which,

other earths, being combined with muriatic acid, remain

\* Ekeberg, Ann. de Chim. Iliii. 277. + Fourcrey, ii. 159. . Anne de Chien, zxvi. IS C. A Rateste, W. Sec.

### ZIRCONIA ....

respect it agrees with yttria; but it is about five times more soluble in carbonate of ammonia than that earth.

It combines with all the acids, and forms with them sweet-tasted salts \*, as is the case also with yttria.

Mr Davy tried to decompose glucina by the same means as have been related in the first section of this Chapter with respect to alumina. The effect was the same. We have reason therefore to believe that it is a metallic peroxide. Mr Davy proposes to call its base glucium.

is was detected. Owing probably to the scarcity of the

proth, or to verify his discovery, whe 1795 he published his analysis of the VI oTDES hother mineral from the same island, in which he also detected a large nobling it talt exter OF ZIRCONIA. , sings is to notice induce clicinists to targetheir attention to the subject d.

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Among the precious stones which come from the island History. of Ceylon, there is one called jargon or zircon, which is possessed of the following properties. dt of malinie have

Its colour is various; grey, greenish-white, yellowish, reddish-brown, and violet. It is often crystallized, either in right angular quadrangular prisms surmounted with pyramids, or octahedrons consisting of double quadrangular pyramids. It has generally a good deal of lustre, at least internally. It is mostly semitransparent. Its hardness is from 10 to 16: Its specific grawity from 4.416 to 4.7 t. or to state of spirit find

It loses scarcely any of its weight in a melting heat ;

\* Hence the name glucina, from yhuxos, stueet. 

Chap. IV.

Composition.

### EARTHS PROPER.

Book II. Division I.

for Klaproth, who analysed it in 1789, found that 300' grains, after remaining in it for an hour and a half, were only one-fourth of a grain lighter than at first \*. Neither was it attacked either by muriatic or sulphuric acid, even when assisted by heat. At last, by calcining it with a large quantity of soda, he dissolved it in muriatic acid, and found that 100 parts of it contained 31.5 of silica, 0.5 of a mixture of nickel and iron, and 68 of a new earth, possessed of peculiar properties, which has received the name of zirconia, from the mineral in which it was detected. Owing probably to the scarcity of the zircon, nobody attempted to repeat the analysis of Klaproth, or to verify his discovery. In 1795 he published his analysis of the byacinth, another mineral from the same island, in which he also detected a large proportion of zirconia, expressing his hopes that it would induce chemists to turn their attention to the subject +. This analysis induced Guyton Morveau, in 1796, to examine the hyacinths of Expailly in France. They proved similar to the hyacinths of Ceylon, and contained the proportion of zirconia indicated by Klaproth 1. These experiments were soon after repeated, and the nature of the new earth still further examined by Vauquelin §.

Preparation. Zirconia has hitherto been found only in the zircon and hyacinth. It may be obtained pure by the following process: Reduce the mineral to powder, mix it with thrice its weight of potash, and fuse it in a crucible. Wash the mass in pure water till the whole of

\* Jour. de Phys. XXXVi. 180.

+ Beitrage, i. 23%.

- \$ Ann. de Chim. xxi. 72.
- § Ibid. xxii. 158. and Jour. de Min. An. v. 97.

# ZIRCONIA.

the potash is extracted; then dissolve the residuum as far as possible in diluted muriatic acid. Boil the solution to precipitate any silica which may have been dissolved; then filter, and add a quantity of potash. The zirconia precipitates in the state of a fine powder.

2. Zirconia, thus prepared, has the form of a fine Properties. white powder, which feels somewhat harsh when rubbed between the fingers. It has neither taste nor odour. It is infusible before the blowpipe; but when heated violently in a charcoal crucible, it undergoes a kind of imperfect fusion, acquires a grey colour, and something of the appearance of porcelain. In this state it is very hard, its specific gravity is 4.3, and it is no longer soluble in acids.

Zirconia is insoluble in water ; but it has a considerable affinity for that liquid. When dried slowly, after being precipitated from a solution, it retains about the third of its weight of water, and assumes a yellow colour, and a certain degree of transparency, which gives it a great resemblance to gum arabic \*.

3. It does not combine with oxygen, simple combustibles, azote, nor metals; but it has a strong affinity for several metallic oxides, especially for oxide of iron. from which it is very difficult to separate it.

It is insoluble in liquid alkalies, neither can it be fused along with them by means of heat; but it is soluble in alkaline carbonates.

4. Scarcely any experiments have been made to ascertain its affinity for the different earths. It is known, however, that a mixture of alumina and zirconia is capable of fusion.

\* Vauquelin, Ann. de Chim. IXii. 158.

Chap. IV.

#### EARTHS PROPER.

Book II. Division I. Zirconia combines with all the acids, and forms salts, which have a peculiar astringent taste, and are many of them insoluble in water.

This earth has not hitherto been applied to any use. Its scarcity, and the difficulty of procuring it in a state of purity, exclude it at present from any chance of being employed for the purposes of domestic economy.

Composition. The same attempts were made by Mr Davy to decompose zirconia as those made upon alumina and glucina, and with similar results. The metallic base he proposes to call zirconium.

of the appearance of porcelain. In this state it is very

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Inble in acids.

Zirconia is insoluble in water : but it has a considerable affinity for that i.YuiTDJE hen dried slowly, after being precipitated from a solution, it retains about the third of its weight of water, and assumes a yellow colour, and a certain degree of uransparency, which gives

History.

THERE is a very hard white stone, known by the name of quartz, very common in almost every part of the world. Sometimes it is transparent and crystallized, and then is called rock crystal. Very frequently it is in the form of sand. As this stone, and several others which resemble it, as flint, agate, calcedony, &cc. have the property of melting into a glass when heated along with fixed alkali, they were classed together by mineralogists under the name of vitrifiable stones. Mr Pott, who first described their properties in 1746, gave them the name of siliceous stones, on the supposition that they were all chiefly composed of a peculiar earth called siliceous earth or silica. This earth was known to Glauber, who describes the method of obtaining it : but it Chap. IV. was long before its properties were accurately ascertained. Geoffroy \* endeavoured to prove that it might be converted into lime, and Pott + and Baumé # that it might be converted into alumina: but these assertions were refuted by Cartheuser §, Scheele ||, and Bergman ¶. To this last chemist we are indebted for the first accurate detail of the properties of silica \*\*.

1. Silica may be obtained pure by the following pro- Prepara cess: Mix together, in a crucible, one part of pounded fint or quartz, and three parts of potash, and apply a heat sufficient to melt the mixture completely. Dissolve the mass formed in water, saturate the potash with muriatic acid, and evaporate to dryness. Towards the end of the evaporation the liquid assumes the form of a jelly; and when all the moisture is evaporated, a white mass remains behind. This mass is to be washed in a large quantity of water and dried ; it is then silica in a state of purity.

2. Silica, thus obtained, is a fine white powder, with- Properties out either taste or smell. Its particles have a harsh feel. as if they consisted of very minute grains of sand. Its specific gravity is 2.66 ++.

It may be subjected to a very violent heat without undergoing any change. Lavoisier and Morveau exposed it to the action of a fire maintained by oxygen gas without any alteration 11. Saussure indeed has suc-

11 I DET SCROTHC FTAVI	C Treat, amoundance to
* Mem. Par. 1746, p. 286,	† Litbogn. p. 3. Præf.
\$ Man. de C'bym.	§ Miner Abb.
Scheele, i. 191.	advert to work to
¶ Sur les Terres Geoponiques, 1773	, Opuse. v. 59.
** Opusc. ii. 26.	tt Kirwan's Min. i. 10.
tt Jour. de l' Ecole Polytechn. 1. iii.	299.
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# EARTHS PROPER.

Book II. Division I. ceeded in fusing, by means of the blowpipe, a portion of it so extremely minute as scarcely to be perceptible without a glass. According to the calculation of this philosopher, the temperature necessary for producing this effect is equal to 4043° Wedgewood.

Action of water. 3. It is insoluble in water except when newly precipitated, and then one part of it is soluble in 1000 parts of water \*. It has no effect on vegetable colours.

It is capable of absorbing about one-fourth of its weight of water, without letting any drop from it; but on exposure to the air, the water evaporates very readily †. When precipitated from potash by means of muriatic acid and slow evaporation, it retains a considerable portion of water, and forms with it a transparent jelly; but the moisture gradually evaporates on exposure to the air.

Silica may be formed into a paste with a small quantity of water; this paste has not the smallest ductility, and when dried forms a loose, friable, and incoherent mass  $\ddagger$ .

Silica is capable of assuming a crystalline form. Crystals of it are found in many parts of the world. They are known by the name of rock crystal. When pure they are transparent and colourless like glass: they assume various forms; the most usual is a hexagonal prism, surmounted with hexagonal pyramids on one or both ends, the angles of the prism corresponding with those of the pyramids. Their hardnes is very great, amounting to 11. Their specific gravity is 2.653 ||.

\* Kirwan's Min. i. 10. † lbid. ‡ Scheele. || Kirwan's Min.-i. 242.

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There are two methods of imitating these crystals by art. The first method was discovered by Bergman. He dissolved silica in fluoric acid, and allowed the solution to remain undisturbed for two years. A number of crystals were then found at the bottom of the vessel, mostly of irregular figures, but some of them cubes with their angles truncated. They were hard, but not to be compared in this respect with rock crystal \*.

The other method was discovered by accident. Professor Seigling of Erfurt had prepared a liquor silicum, which was more than usually diluted with water, and contained a superabundance of alkali. It lay undisturbed for eight years in a glass vessel, the mouth of which was only covered with paper. Happening to look to it by accident, he observed it to contain a number of crystals; on which he sent it to Mr Trommsdorf, professor of chemistry at Erfurt, who examined it. The liquor remaining amounted to about two ounces. Its surface was covered by a transparent crust, so strong that the vessel might be inverted without spilling any of the liquid. At the bottom of the vessel were a number of crystals, which proved on examination to be sulphate of potash and carbonate of potash +. The crust on the top consisted partly of carbonate of potash, partly of crystallized silica. These last crystals had assumed the form of tetrahedral pyramids in groupes; they were perfectly transparent, and so hard that they struck fire with steel t.

4. Silica neither combines with oxygen, with the

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Action of simple substances.

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\* Bergman, ii. 32.

† Potash combined with sulphuric acid and carbonic acid,

† Nicholson's Journal, i. 217.

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Chap. IV

# EARTHS PROPER.

Book II. Division I.

Action of alkalies.

simple combustibles, nor with metals; but it combines with many of the metallic oxides by fusion, and forms various coloured glasses and enamels.

5. Azote has no action on silica; neither has muriatic acid when the silica is in a solid state; but when the silica is combined with an excess of alkali, muriatic acid dissolves the compound, and forms a permanent solution. By concentrating this solution, the silica separates from it in the form of a jelly.

6. There is a strong affinity between silica and fixed alkalies. It may be combined with them either by fusing them along with it in a crucible, or by boiling the liquid alkalies over it. When the potash exceeds the silica considerably, the compound is soluble in water, and constitutes what was formerly called *liquar silicum* and now sometimes *silicated potash* or *soda*. When the silica exceeds, the compound is transparent and colourless like rock crystal, and is neither acted on by water, air, nor (excepting one) by acids. This is the substance so well known under the name of glass.

Silica is not acted on by ammonia, whether in the gaseous or liquid state.

Of barytes.

7. There is a strong affinity between barytes and silica. When barytes water is poured into a solution of silica in potash, a precipitate appears, which is considered by Morveau as the two earths in a state of combination \*. Barytes and silica may be combined by means of heat. The compound is of a greenish colour, and coheres but imperfectly  $\dagger$ . The effect of heat on va-

> \* Morveau, Ann. de Chim. xxxi. 250. † Vauquelin, ibid. xxix. 271.

# SILICA.

rious mixtures of barytes and silica will appear from the following experiments of Mr Kirwan \*.

Proportions.	Heat.	Effect.
80 Silica 20 Barytes	150° Wedg.	A white brittle mass.
75 Silica 20 Barytes	150	A brittle hard mass, semi- transparent at the edges.
66 Silica 33 Barytes	150	Melted into a hard, some- what porous porcelain mass.
50 Silica 50 Barytes	148 day A	A hard mass not melted.
20 Silica 80 Barytes	148	The edges were melted into a pale greenish mat- ter between a porcelain and enamel.
25 Silica 15 Barytes		Melted into a somewhat
33 Silica 66 Barytes	150	Melted into a yellowish and partly greenish white porous porcelain.

Strontian and silica combine with each other nearly Strontian. 

There is also an affinity between silica and lime. Line. When lime-water is poured into a solution of silica in a potash, a precipitate appears, as Stucke discovered. This precipitate is a compound of silica and lime +. These

Kirwan's Miner. i. 17.

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+ Gadolin, Ann. de Chim. xxii. 110 .- Morveau, ibid. xxxi. 250.

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#### EARTHS PROPER.

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two earths may be combined also by means of heat. They form a glass, provided the quantity of lime be not inferior to that of silica. The effect of heat upon these earths, mixed in various proportions, will appear from the following experiments of Mr Kirwan \*.

Proportions.	Heat.	Effect.		
50 Lime 50 Silica	150° Wedg.	Melted into a mass of a white colour, semitransparent at the edges, and striking fire, though feebly, with steel: it was somewhat between porcelain and enamel.		
80 Lime 20 Silica	156	A yellowish white loose powder.		
20 Lime 80 Silica		Not melted, formed a brit- tle mass.		

Magnesia,

Equal parts of magnesia and silica melt with great difficulty into a white enamel when exposed to the most violent heat which can be produced +. They are infusible in inferior heats in whatever proportion they are mixed ‡.

And alumina. There is a strong affinity between alumina and silica. When equal portions of silicated and aluminated potash are mixed together, a brown zone immediately appears, which may be made, by agitation, to pass through the whole liquid. After standing about an hour, the mixture assumes the consistence of jelly ||.

\* Kirwan's Min. i. 56. + Lavoisier, Mem. Por. 1787, p. 598.

- t Achard, Mem, Berl. 1780, p. 33.
- Morveau, Ann. deChim. xxxi. 249.

When formed into a paste with water, and dried, they cohere, and contract a considerable degree of hardness. When baked in the temperature of 160° Wedgewood, they become very hard, but do not fuse\*. Achard found them infusible in all proportions in a heat probably little inferior to 150° Wedgewood. But when exposed to a very strong heat, they are converted into a kind of opaque glass, or rather enamel. Porcelain, stoneware, brick, tiles, and other similar substances, are composed chiefly of this compound. Mixtures of silica and alumina in various proportions constitute *clays*; but these are seldom uncontaminated with some other ingredients.

It follows from the experiments of Achard, that equal parts of lime, magnesia, and silica, may be melted into a greenish coloured glass, hard enough to strike fire with steel; that when the magnesia exceeds either of the other two, the mixture will not melt; that when the silica exceeds, the mixture seldom melts, only indeed with him in the following proportions; three silica, two lime, one magnesia, which formed a porcelain; and that when the lime exceeds, the mixture is generally fusible †.

A mixture of silica and alumina may also be combined with barytes or strontian by means of heat. The mixture melts readily into a greenish coloured porcelain  $\ddagger$ .

From the experiments of Achard and Kirwan, we learn, that in mixtures of lime, silica, and alumina, when the lime exceeds, the mixture is generally fusible

\* Kirwan's Min. i. 58.

As it approaches in some of

+ Mem. Berl. 1780, p. 33. and Jour, de Phys. xxiv. 1 Kirwan.

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#### EARTHS PROPER.

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either into a glass or a porcelain, according to the proportions. The only infusible proportions were,

2 3 Lime 1 1 Silica 2 2 Alumina.

That if the silica exceeds, the mixture is frequently fusible into an enamel or porcelain, and perhaps a glass; and that when the alumina exceeds, a porcelain may often be attained, but not a glass \*.

As to mixtures of magnesia, silica, and alumina, when the magnesia exceeds, no fusion takes place at 150°. When the silica exceeds, a porcelain may often be attained; and three parts silica, two magnesia, and one alumina form a glass. When the alumina exceeds, nothing more than a porcelain can be produced  $\dagger$ .

Achard found that equal parts of lime, magnesia, silica, and alumina, melted into a glass. They fused also in various other proportions, especially when the silica predominated.

Silica differs from all the other earths in not combining with any of the acids except the fluoric, phosphoric, and boracic; to which perhaps we may add the muniatic.

Silica is one of the most important of the earths. It is the chief ingredient of those stones which seem to constitute the basis of this terrestrial globe. It is an essential ingredient in mortar, in all kinds of stoneware, and in glass.

Composi-

Mr Davy made many experiments to ascertain the composition of silica, and has rendered it probable that it is a metallic peroxide. As it approaches in some of

# Kirwan's Min. i. 73. + Ibid. i. 72.

# SILICA.

its properties to various insoluble salts, he thought it requisite, in the first place, to inquire whether it might not be a compound of an unknown acid and earth. But when exposed to the action of a powerful galvanic battery it was not decomposed; of course there was no reason for considering it as propable that it was of a saline nature. On the supposition that it was a metallic peroxide, it was exposed to experiments precisely similar to those formerly described, when treating of the decomposition of alumina, and the results were exactly the same. Hence there is reason to consider it as a compound of oxygen and a peculiar metal, though the experiments cannot be considered quite decisive. To the supposed metal Mr Davy proposes to give the name of *tilicium*.

Song before chemistry became an accurate science. We treed not threefore be surprized that their meaning was somewhat wague; and that as chamical substance mulsiphed, it became difficult to ascertain to which of the two they ought to be assigned. Two properties appear to have been considered as ressential to the alkalies. 1. They were expende of combining with acids, and of

depriving them of their scidiry, while they themselves

lost their characteristic propetition, or were exclusived, g. They were soluble in ware, sinsolubility in water, or arrive, as the characteristic truncal, joined to incombudfibility, which characteristic of an earth Thisse group thes acroad to arrange tendy discovered Thisse group thes acroad to arrange tendy discovered substances, at they combared with active and ware sotable in water, they combared with active and ware sothat is in a soluble in water, they took their station anong the certing. Here wore as a common an discovered, anong the certing Herm work, as soon as discovered, anong the certing the work of the solution of the source of the station anong the certing Herm work, as soon as discovered,

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# REMARKS ON

quisite, in the first place, to inquire whether it might

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> not be a construction on indentification with a static batwhen exposed to the action of a powerful galvanic battery it was not decomposed of course there was no reason to considering it .V. . **QAHD** that it was of a salino means. On the supposition that it was a metallic perto those a construction of that it was a metallic perto those a construction of the supposition that it was a metallic perto those a construction of the supposition that it was a metallic perto those a construction of the supposition that it was a metallic perto those a construction of the supposition of the supposet of the supposition of the supposet of the supposet of the supposition of the supposet of the supposet

The terms alkali and earth were brought into use long before chemistry became an accurate science. We need not therefore be surprized that their meaning was somewhat vague; and that as chemical substances multiplied, it became difficult to ascertain to which of the two they ought to be assigned. Two properties appear to have been considered as essential to the alkalies. 1. They were capable of combining with acids, and of depriving them of their acidity, while they themselves lost their characteristic properties, or were neutralized. 2. They were soluble in water. Insolubility in water, or aridity, as the chemists termed it, joined to incombustibility, was considered as characteristic of an earth. These properties served to arrange newly discovered substances. If they combined with acids, and were soluble in water, they were considered as alkalies; but if they were insoluble in water, they took their station among the earths. Hence soda, as soon as discovered, was denominated an alkali, while lime, barytes, stron-

Original meaning of elkali and earth.

#### ALKALIES AND EARTHS.

tian, &c. were successively placed among the earths ; for the solubility of the first of these bodies in water was long misunderstood. The whole of the lime was not considered as soluble in water, but a certain portion of it which approached alkalies in its nature ; and though this error had been rectified before the discovery of strontian, yet analogy led chemists to class this body along with lime and barytes, which had already taken 

The alkalies naturally subdivided themselves into Subdivifixed and volatile; a distinction made at an early pe- them. riod, sufficiently correct, and attended with many advantages. The subdivision of the earths into alkaline and proper was a much later improvement. Indeed it was only after the earths had been examined in a state of tolerable purity that such a subdivision was possible. Those earths that possessed all the characteristics of alkalies, excepting that of being very soluble in water, were denominated alkaline, while those that were incapable of neutralizing acids, and which were insoluble in water, were considered as more peculiarly entitled to the name of earth. This subdivision was obviously intended to correct the too great vagueness of the terms earth and alkali as originally applied. It appears more proper than some other methods that have been practised for the same purpose. Fourcroy, for instance, classes barytes and strontian with the alkalies. No fault can be found with this arrangement, because the division of these bodies into earths and alkalies is perfectly arbitrary. But surely if barytes and strontian be placed among alkalies, lime ought not to be excluded ; for barytes and strontian do not possess a single alkaline property of which lime is destitute. And if lime

Bertheller's definition of

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#### REMARKS ON

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Berthollet's definition of alzali.

be reckoned among the alkalies, no good reason can be given why magnesia should be excluded. The truth is, that these bodies graduate into each other so nicely that they can scarcely be placed in different classes. This is a sufficient reason for preferring the common division to the new one proposed by Fourcroy.

Berthollet has suggested another definition of alkalies, which appears to me much more correct than that of According to him, all bodies capable of Fourcroy. neutralizing acids are entitled to the name of alkalies. Alkalinity is the property of neutralizing acids, and acidity that of neutralizing alkalies. According to this definition, the alkalies, both fixed and volatile, and the alkaline earths, ought to be considered as alkalies. Though objections might perhaps be started to this definition, as is the case indeed with all definitions whatever, yet it must be allowed to be much more precise, and gives us a more satisfactory notion of alkalinity than any that preceded it. But if the capacity of neutralizing acids constitutes alkalinity, it is obvious that those bodies must possess most of that property, which are most capable of neutralizing acids, or which are capable of neutralizing the greatest quantity of acid. According to this doctrine the alkalies arrange themselves in the following order; that one standing first which neutralizes the greatest quantity of acid \*; and met heat

Ammonia, laste ban este al estela Magnesia, dr. bagot of arealast eren ei artistile t Lime, tan orne estival seaft loursielvib feetle arbitrary. 12 Hut succes if baneters

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\* Berthollot, Statique Chemique, i. p. 125. The order was established from the experiments of Kirwan,

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## ALKALIES AND EARTHS.

Soda, Potash, Strontian, Barytes.

The earths proper combine with acids, but do not neutralize them \*.

The alkalies (using the word in Berthollet's sense) do not combine with oxygen. They do not act upon hydrogen nor carbon; but they combine with sulphur, and unite with phosphorus, or at least act upon it with considerable energy. Their action upon metals is not very remarkable. Some metallic oxides they dissolve, while upon others they have no effect. They are all more or less soluble in water except magnesia; but the alkaline earths much less so than the others.

The earths proper do not unite with oxygen, at least as far as has been ascertained in a satisfactory manner. They do not unite with simple combustibles nor metals, and have a much less tendency to enter into combinations than the alkalies.

The following Table exhibits some of the most remarkable characters of the alkaline and proper earths  $\dagger$ .

triking resemblance to exch other.

\* To this there are some exceptions. This constitutes one of the defects of Berthollet's definition.

† In this Table several properties have been placed, with which the reader will become acquainted by perusing the subsequent part of this Work. It was thought worth while to add then, that the Table might contain the most important properties of the earths collected together.

After Leing at tells

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Earths.	Solubility in 1 of water.	Tinge vegetable blues.green.	Soluble in potash.	Soluble in carbonate of ditto.	Soluble in carbonate of ammonia.	Soluble in nurratic- acid *.	Precipitated by prussiate of potash.	Precipitated by tan.	Precipitated by hy- drosulphurets.	Precipitated by suc- cinates.	
Barytes	0.050	1	i B	ow	ent.	i	r) 2	alla's	lle	1	
Stront.	0.005	2	iary)	odi :	27.2 111	2	in:	lon	en	2	en ed
Lime	0.002	3	5t ]	20	etric	3	pha	ntr	1031	3	TR.
Magnes.	0.000	4	olil	neta	581	4		Ical	eme	17	97 97
Alum.	0.000	3593 (111 1	1	1 37	211 V	5	and.	101		SIII:	1
Yttria	0.000	a se	an u	10	1	6	I	1	ie 51	ilino -	la.
Glucina	0.000	eine sinte	2	2	2	7	0.00	2	as b	4	2.5
Zircon.	0.000	bust	cota	3	SITT	8	2	3	2	Ver	T
Silica	0.000		3			.egil		the	nor	1 11	13

It deserves attention, that a considerable number of these bodies may be divided into pairs, which have a striking resemblance to each other. These pairs are,

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1.	Potash Soda	3.	Yttria Glucina
2.	Barytes Strontian	4.	Alumina Zirconia

But the resemblance between alumina and zirconia, which constitute the last pair, is not so close as that

# After being precipitated.

# ALKALIES AND EARTHS.'

between the bodies which form the other pairs. Ammonia, magnesia, and silica, have none of them corresponding substances.

Now that the secret of the composition of the alkalies and earths has been revealed, it is obvious that they all belong to the same class of substances, and that they ought to be placed among the metallic oxides. Thus the conjecture of the old chemists has been verified with respect to the earths; while the constitution of the alkalies has turned out different from every previous conjecture.

or the science of chemistry had made sufficient progress, this division would comprehend all the comprushed which the simple confinable bodies are capable of forming with each officer. But we are not yet sufficiently acquainted with all of these combinations to be able to detail them at length ; and many substances known to exist and to belong to this division, have not been sufficiently extmitted to enable us to asign them their proper winas ation, 50 We cannon therefore, mitrothee all primary compounded into this division, but those only, in the undrais of which chemistry has made tonsiderable nou-Last Device a line of the starting the strangeness within The contrable bodie were divided into four classes i namely, Ouroand Cownerstance, Pronumerinities and Markes, o'Oregen unites with all the bodies belo more disor bab ; exacto would realth out of dataset tions it units in variant propertions. United in one transis is allowed a the of the removed president his meak abox, in which the name of our falling tree and

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# PRIMARY COMPOUNDS.

Book II. Division II. between the bodies which form the other pairs. Ammonia, megnesis, and silics, have none of them correponding substances:

Now that the secret of the composition of the alltailes and carify has been **AP** cMOISIVIC vious that they all belong to the same class of substances, and that they ought to be placed among the metallic oxides. Thus the conjecture of the old chemists has been verified with respect to **SCONUONMOON YRAMING** it he alkalies has converted chemists from every previous conisoture.

IF the science of chemistry had made sufficient progress, this division would comprehend all the compounds which the simple confinable bodies are capable of forming with each other. But we are not yet sufficiently acquainted with all of these combinations to be able to detail them at length; and many substances known to exist, and to belong to this division, have not been sufficiently examined to enable us to assign them their proper situaation. We cannot, therefore, introduce all primary compounds into this division, but those only, in the analysis of which chemistry has made considerable progress.

The confinable bodies were divided into four classes; namely, OXYGEN, COMBUSTIBLES, INCOMBUSTIBLES, and METALS. Oxygen unites with all the bodies belonging to the other three classes; and with most of them it unites in various proportions. United in one proportion, it forms a set of bodies incapable of neutralizing alkalies, to which the name of *oxide* has been assigned; united in another proportion, it forms a set of

#### PRIMARY COMPOUNDS.

bodies called *acids*, capable of neutralizing alkalies. Each of these sets comprehends under it a variety of bodies of great importance in chemistry, and which, therefore, deserve to be examined with attention. The combustibles unite with each other, and form a very numerous class of bodies still capable of combustion, and which, therefore, may be called *compound combustibles*. They unite also with *incombustibles* and with *metals*. The incombustibles, as far as we know, do not unite with *each other*, nor with the *metals*; but the metals combine together, and form compounds called *alloys*. Hence we see that the primary compounds naturally divide themselves into the six following classes:

1. Oxides;

Division.

- 2. Acids;
- 3. Compound combustibles;
- 4. Combinations of combustibles and incombustibles;

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- 5. Combinations of combustibles and metals;
- 6. Combinations of metals with each other.

Many the whole of the

Of these classes, the two last, in the present state of the science, are of least importance. The compounds belonging to them are scarcely entitled to a separate examination, and for that reason were introduced in the first Book of this Work, during the examination of the simple substances, of which they are compounds. As to the fourth class, we are at present acquainted only with one substance which we know to belong to it. That substance is *ammonia*, which was arranged with the fixed alkalies and earths, for reasons formerly specified. The first three classes of primary compounds alone remain to be examined. They shall form the subject of the following chapters.

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CHAP. I.

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# OF OXIDES.

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Combination of oxygen

WE have seen already that oxygen combines with bodies in various proportions, constituting a variety of compounds with almost every substance with which it is capable of uniting. Now the whole of the compounds into which oxygen enters may be divided into two sets: 1. Those which possess the properties of acids; and, 2. Those which are destitute of these properties. The first set of compounds are distinguished by the term acids; to the second, the term oxide has been appropriated. By oxide, then, is meant a substance composed of oxygen and some other body, and destitute of the properties which belong to acids. It is by no means uncommon to find a compound of the same base and oxygen belonging to both of these sets, according to the proportion of oxygen which enters into the compound. In all these cases, the smaller proportion of oxygen constitutes the oxide ; the larger the acid. Hence it fol--

lows, that oxides always contain less oxygen than acids with the same base.

The oxides, then, which we have to examine in this chapter, are combinations of oxygen with the simple combustibles, the simple incombustibles, and the metals; substances which may be denominated the bases of the oxide. Now the oxides differ considerably from each other, according to the nature of the base and the manner in which the combination has been formed. Some of them are *products* of combustion, others of them are *combustible*, while a third set are *supporters* of combustion. The metallic oxides, which have been already examined, belong partly to the first and partly to the last of these classes. The following Table exhibits a view of the different oxides (omitting the metallic) arranged under their respective classes.

# I. OXIDE PRODUCTS.

Base. Name. Hydrogen.....Water.

II. COMBUSTIBLE OXIDES.

Carbon.....Carbonic oxide. Phosphorus.....Oxides of phosphorus. Sulphur....Oxides of sulphur.

III. OXIDE SUPPORTERS.

Azote....... { Nitrous oxide. Nitric oxide. Muriatic acid......Oxymuriatic acid.

The examination of these oxides shall occupy our attention in the following Sections.

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# I. OXIDE PRODUCTS.

Hydrogen differs from the other simple combustibles in several respects. It is the only one of them which is capable of uniting with only a single dose of oxygen, and of forming a compound entirely destitute of acid properties. This compound is *Water*. It is formed by combustion, and is therefore a *product*. All the other products into which the simple combustibles enter are *acids*. The only oxide product, then, at present known (exclusive of the metallic) is *water*.

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# SECT. I.

STOURDS PRINT PROPERTY.

# OF WATER.

THIS well-known liquid is found in abundance in every part of the world, and is absolutely necessary for the existence of animals and vegetables. When pure, in which state it can be obtained only by distillation, it is transparent, and destitute of colour, taste, and smell.

Weight.

1. As this liquid, from the ease with which it may be procured in a state of purity, has been chosen for a standard by which the comparative weight of all other bodies may be estimated, it becomes of the greatest importance to ascertain its weight with precision : But its density varies with the temperature. At the temperature of  $36^\circ$ , its density is a maximum; and for the two or three degrees on each side of  $36^\circ$ , the varia-

tion of its density is scarcely perceptible. Now, from the experiments of Lefevre Gineau, performed with great care, in order to ascertain the weight of the millegramme, it follows, that, at the temperature of 40°, a French cubic foot of distilled water weighs 70lbs. and 223 grains French = 529452.9492 grains troy\*. Therefore an English cubic foot, at the same temperature, weighs 437102.4946 grains troy, or 999.0914161 ounces avoirdupois. Hence a cubic inch of water at 40° weighs 252.953 grains, and at 60°, 252'72 grains. A cubic foot of water, at the temperature of 55°, weighs, according to the experiments of Professor Robison of Edinburgh, 998.74 avoirdupois ounces, of 437.5 grains troy each, or only 1.26 ounces less than 1000 avoirdupois ounces : so that rain water, at the same temperature, will weigh pretty nearly 1000 ounces. The specific gravity of water is always supposed = 1.000, and it is made the measure of the specific gravity of every other body.

2. When water is cooled down to 32°, it assumes Ice. the form of ice. If this process goes on very slowly, the ice assumes the form of crystalline needles, crossing each other at angles either of 60° or 120°, as Mr de Mairan has remarked; and it has been often observed in large crystals of determinate figures †. Ice, while kept at a temperature considerably below 32°, is very hard, and may be pounded into the finest dust. It is elastic. Its specific gravity is less than that of water.

3. When water is heated to the temperature of 212°.

Steam.

\* Jour. de Pbys. xlix. 171.

See observations on this subject by Grew. Phil. Trans. Abr. ii. 54-

Chap. I.

#### OXIDES.

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it boils, and is gradually converted into steam. Steam is an invisible fluid like air, but of a less specific gravity. It occupies about 1800 times the space that water does. Its elasticity is so great, that it produces the most violent explosions when confined. It is upon this principle that the steam-engine has been constructed.

The phenomena of boiling are owing entirely to the rapid formation of steam at the bottom of the vessel. The boiling point of water varies according to the pressure of the atmosphere. In a vacuum water boils at 70°; and when water is confined in Papin's digester, it may be almost heated red hot without boiling. The mixture of various salts with water affect its boiling point considerably. Mr Achard made a number of experiments on that subject; the result of which may be seen in the following TABLES \*.

Boiling point affected by salts.

CLASS I. Salts which do not affect the Boiling Point.

Sulphate of copper.

CLASS II. Salts which raise the Boiling Point

saturated s lution of	Muriate of soda Sulphate of soda Sulphate of potash Nitrate of potash Boracic acid Carbonate of soda	Raises the boiling point	10·35° 5·6 0·9 3·5 2·2 2·35
			CILL, MILLING

This augmentation varies with the quantity of salt

\* Trans. Berlin, 1785.

#### WATER.

dissolved. In general, it is the greater the nearer the Chap. I. solution approaches to saturation.

# CLASS III. Salts which lower the Boiling Point.

Borax, Saturated solution of	nunanodi.
Borax, ¿ ing point	1.320°
Saturated solution of	0.22
Sal hat G	2.47
Sulphate of magnesia, { In a small quantity Saturated solution of	1.1
( A very small quantity of	0.0
Alum, A greater quantity	0.7
Alum, A greater quantity A saturated solution of	0.0
G 1 1 . C1' .	
Sulphate of lime, Sulphate of zinc, Sulphate of iron, in any proportion,	0.45
Sulphate of iron, ( in any proportion, )	0.22
	1.24

# CLASS IV.

Muriate of ammonia,

Carbonate of Small quantity of, lowers do. 0.45 ? Saturated solution of, raises do. 11.2

potash,

Water was once supposed to be incompressible; but the contrary has been demonstrated by Mr Canton. The Abbé Mongez made a number of experiments. long after that philosopher, on the same subject, and obtained similar results.

4. Water is not altered by being made to pass through Action of a red hot tube. Heat does not seem capable of decomposing it; neither is it affected by the action of light.

5. It has the property of absorbing atmospheric air; and it always contains a portion of it when it has been

heat.

Absorbs

#### · OXIDES.

Book H. Division H.

How air may be sc-

parated

from it.

exposed to the atmosphere. The greater part of this air is driven off by boiling : but, from the experiments of Dr Priestley, it appears that the whole of it is not separated; nor can it be completely separated without great difficulty. Water owes its agreeable taste to the presence of air; hence the insipidity of boiled water, It absorbs oxygen gas in preference to air, and nearly in the same proportion, as was first ascertained by Scheele.

Mr Driessen has shown, that in order to free water from air, it must be boiled at least for two hours, and kept in a flask with its mouth inverted over mercury. If it be exposed to the air, after this process, for ever so short a time, it immediately absorbs some air ; a proof of the strong affinity which it has for that fluid \*. This philosopher has pointed out the following method of ascertaining whether water be perfectly free from air. Tinge the water blue with litmus, fill a flask with it, invert the flask under water, and introduce into it pure nitrous gas till about  $\frac{1}{20}$  of the vessel is filled. If the water contain air, a portion of the nitrous gas will combine with its oxygen, and be converted into nitric The consequence of which will be, that the litacid. mus will assume a red colour, Even the proportion of air in the water may be estimated by the quantity of ammonia necessary to restore the blue colour to the litmus. If the litmus retains its blue colour, we may be certain that the water which we try contains no sensible portion of air +. It is proper to remark, however, that this experiment does not succeed in a satis-

# Phil. Mag. 18-3, XV. 252.

+ Ibid.

5. It be

posing it; neither is it thened I

factory manner, unless an unusual quantity of oxygen gas be present. No effect is produced when nitrous gas is agitated with good spring water.

6. Water has no action on the simple combustibles while cold, nor does it combine with any of them. Hydrogen does not act upon it even at a red heat; but charcoal at that temperature decomposes it, forming carbonic acid, and various species of heavy inflammable air. The action of phosphorus at a red heat has not been tried. Sulphur, as far as is known at present, does not decompose it.

7. Of the metals, iron, zinc, antimony, and tin, decompose it when assisted by heat; silver, gold, copper, and platinum, have no effect upon it. The action of the other metals at a red heat has not been tried\*.

8. Water dissolves the alkalies and alkaline earths. The earths proper are insoluble in it. It dissolves also acids and salts, and is capable of combining with a great variety of bodies.

9. Water has the property of uniting with bodies in two different ways. Some it dissolves; the compound forms. becomes liquid, like water. In this way it unites with common salt, with sugar, and a vast number of other bodies. Other substances combine with it without losing their solidity. The water in this case loses its liquid form, and assumes that of the substance to which it has united. In this way it unites to lime, to alumina, to many saline bodies, and to a variety of metallic oxides. When the compound of water with another substance remains liquid, the proportion of water is un-

\* Mem, Par. 1781. p. 273.

hereitioned.

Chap. I.

Action of the simple combustibles,

Of the metals,

Alkalies and earths.

Water combines in two

#### OXIDES.

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Hydrates.

limited; but when the combination formed is solid, the water combines always in a certain determinate proportion.

To the first of these combinations, or the solutions of bodies in water as they have been termed, considerable attention has always been paid; but the second kind, in which the water assumes a solid form, was very much overlooked, if not altogether neglected, till the attention of chemists was drawn to them by Mr Proust, who has given to such combinations the name of bydrates. Thus the combination of lime and water, usually called slacked lime, is in his language a bydrate of lime: in like manner, the crystals of barytes and strontian are hydrates of these alkaline earths, and crystallized potash and soda are hydrates of the fixed alkalies. Though the term bydrate is in some respects exceptionable, we shall continue to use it, as no other has been suggested. The compounds called bydrates deserve attention, since they differ very considerably in their properties from those bodies with which they have been hitherto confounded. Thus the hydrates of lime, barytes, potash, &c. are very different in several respects from lime, barytes. potash, &c. De china de

Alkaline and earthy hydrates. The hydrates of potash and soda are crystallized, and contain always a determinate proportion of water: according to Proust, about 30 *per cent*. When dissolved in water they occasion cold; whereas the alkalies in the state of powder produce heat. The same observations are applicable to the hydrates of barytes and strontian. The proportion of water which combines with lime is much less considerable than that which enters into the composition of the hydrates just mentioned. Hence the hydrate of lime does not crystallize, but re-

mains usually in the state of a powder. We know, however, that it retains the water with great obstinacy, and that the formation of it is one of the principle causes of the solidification of mortar \*. The hydrate of alumina is no less remarkable for the obstinacy with which it retains its water. It is the substance to which Saussure gave the name of spongy alumina.

But the hydrates of the metallic oxides are the most Metalline. remarkable. They first drew the attention of Proust, and induced him to invent the term hydrate. His observations, as far as regards the bydrate of copper; have been called in question by Berthollet junior +; but his arguments do not appear to me sufficiently conclusive to overturn the ingenious theory of the Spanish chemist. He has demonstrated indeed, that the bydrate of copper usually retains a small portion of acid; but he has not shown that its peculiar properties are owing to that acid, while Proust has made the contrary more than probable, by ascertaining that the properties of the hydrate remain the same, even when the proportion of acid varies, and when it is so far diminished as to be no longer perceptible.

When copper is dissolved in nitric acid, and a suffi- Hydrate of cient quantity of potash added to the solution, a blue powder falls to the bottom, which when sufficiently washed, and carefully dried, coheres together, and forms a brittle mass breaking with a vitreous fracture. This mass is the hydrate of copper. It has an exquisitely disagreeable taste, and acts with great energy upon the

\* See Proust, Jour. de Pbys. lix. 34 .

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copper.

<sup>+</sup> Statique Chemique, il. 455.

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Of iron,

system when swallowed, or even kept in the mouth. When distilled it yields 25 parts of water, and leaves 75 of black oxide of copper.

When the solution of iron in sulphuric acid is treated in the same way, a green powder falls, which is a hydrate of iron. These two hydrates are delicate, and easily lose their water. But some of the other hydrates of the metallic oxides retain their water with great obstinacy. This is the case particularly with the hydrates of nickel and cobalt, which resist the action of a considerable heat \*.

Of tin.

When tin dissolved in muriatic acid is precipitated by potash, a white powder is obtained, which washed and dried in the heat of boiling water is a hydrate of tin. When distilled in a retort it loses 5 per cent. of water, and is converted into protoxide of tin +.

Most of the metallic hydrates are remarkable for the brilliancy of their colours. They are much more easily dissolved by acids than the oxides; and when put into the mouth they affect the organs of taste even more powerfully than the metallic salts.

Gases contain water. 10. All gases in their usual state contain combined with them a quantity of water, which often amounts to a considerable proportion of their weight. Part of this water may be abstracted by exposing the gases to substances which have a strong affinity for water, as dry potash; but part adheres with a great deal of obstinacy, and perhaps cannot be removed by any method in our power.

11. Water was believed by the ancients to be one of

\* Proust, Jour. de Pbyr. Hx. 347.

f Ibid. r. 338.

the four elements of which every other body is compo- Chap. I. sed; and, according to Hippocrates, it was the substance which nourishes and supports plants and animals. That Opinions a-bout the nawater was an unchangeable element continued to be be- ture of walieved till the time of Van Helmont, who made plants ter. grow for a long time in pure water : from which experiment it was concluded, that water was convertible into all the substances found in vegetables. Mr Boyle having digested pure water in a glass vessel hermetically sealed for above a year, obtained a quantity of earthy scales; and concluded, in consequence, that. he had converted it partly into earth \*. He obtained the same earth by distilling water in a tall glass vessel over a slow fire +. Margraff repeated the experiment with the same result, and accordingly drew the same conclusion. But the opinion of these philosophers was never very generally received 1. The last person who embraced it was probably Mr Waselton, who published his experiments on the subject in the Journal de Physique for 1780. Mr Lavoisier had proved, as early as 1773, that the glass vessels in which the distillation was performed lost a weight exactly equal to the earth obtained. Hence it follows irresistibly that the appearance of the earth, which was silica, proceeded from the decomposition of the vessels; for glass contains a large proportion of silica. It has been since shown by Dr Priestley, that water always decom-

+ Ibid. i. 267. \* Shaw's Boyle, iii. 417. \$ See an account of all the facts relating to this subject in Watson's

discover : but

Chemical Essays, iv. 257.

ved that so car again stat was was

Book II. Division II.

History of the discovery of its component parts. poses glass when applied to its surface for a long time in a high temperature.

Water is now known to be an oxide of hydrogen, or a compound of oxygen and hydrogen. As this discovery has almost entirely altered the appearance of the science of chemistry, by furnishing an explanation of a vast number of phenomena which were formerly inexplicable, it will be worth while to give a particular account of the different steps which gradually led to it.

The first person probably who attempted to discover what was produced by burning hydrogen gas was Scheele. He concluded, that during the combustion oxygen and hydrogen combined, and that the product was caloric.

In 1776 Macquer, assisted by Sigaud de la Fond, set fire to a bottle full of hydrogen gas, and placed a saucer above the flame, in order to see whether any fuliginous smoke would be produced. The saucer remained perfectly clean; but it was moistened with drops of a clear liquid, which they found to be pure water \*.

Next year Bucquet and Lavoisier exploded oxygen and hydrogen gas, and made an attempt to discover what was the product; about the nature of which they had formed different conjectures. Bucquet had supposed that it would be carbonic acid gas; Lavoisier, on the contrary, suspected that it would be sulphuric or sulphurous acid. What the product was they did not discover; but they proved that no carbonic acid gas was

\* Macquer's Dictionary, art. Gas inflammable.

#### WATER.

formed, and consequently that Mr Bucquet's hypothesis was ill founded  $\uparrow$ .

In the beginning of the year 1781, Mr Warltire, at the request of Dr Priestley, fired a mixture of these two gases contained in a copper vessel; and observed, that after the experiment the weight of the whole was diminished. Dr Priestley had previously, in the presence of Mr Warltire, performed the same experiment in a glass vessel. This vessel became moist in the inside, and was covered with a sooty substance ‡, which Dr Priestley afterwards supposed to be a part of the mercury used in filling the vessel §.

In the summer of 1781, Mr Cavendish, who had been informed of the experiments of Priestley and Warltire, set fire to 500,000 grain measures of hydrogen gas, mixed with about 21 times that quantity of common air. By this process he obtained 135 grains of pure water. He also exploded 19,500 grain measures of oxygen gas, with 37,000 of hydrogen gas, and obtained 30 grains of water, containing in it a little nitrie acid. From these experiments he concluded that water is a compound .- Mr Cavendish must therefore be considered as the real discoverer of the composition of water. He was the first who ascertained that water is produced by firing oxygen and hydrogen gas, and the first who drew the proper conclusion from that fact." Mr Watt, indeed, had also drawn the proper conclusion from the experiments of Dr Priestley and Mz Warltire, and had even performed a number of experi-

\* Mem. Par. 1981, p. 470. § Phil. Trans. Inxiv: 332.

+ Priestley, v. 395-

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Book II. Division II. ments himself to ascertain the fact before Mr Cavendish had communicated his; but he had been deterred from publishing his theory by some experiments of Dr Prestley, which appeared contrary to it\*. He has therefore a claim to the merit of the discovery; a claim however, which does not affect Mr Cavendish, who knew nothing of the theory and experiments of that ingenious philosopher.

Meanwhile, in the winter 1781-2. Mr Lavoisier, who had suspected that when oxygen and hydrogen gas are exploded, sulphuric or sulphurous acid is produced, made an experiment in order to ascertain the fact, at which Mr Gengembre assisted. They filled a bottle, capable of holding six pints (French), with hydrogen gas, to which they set fire, and then corked the bottle, after pouring into it two ounces (French) of lime-water. Through the cork there passed a copper tube, by means of which a stream of oxygen gas was introduced to support the flame. Though this experiment was repeated three times, and instead of lime water a weak solution of alkali and pure water were substituted, they could not observe any product whatever +. This result astonished Mr Lavoisier exceedingly : he resolved, therefore, to repeat the experiment on a larger scale, and if possible with more accuracy. By means of pipes . furnished with stop-cocks, he put it in his power to supply both gases as they should be wanted, that he might be enabled to continue the burning as long as he thought proper.

The experiment was made by Lavoisier and La Place

# Ibid. 1xxv. 330 ....

+ Mem. Par. 1781, p. 470.

on the 24th of June 1783, in the presence of Messrs Le Roi, Vandermonde, several other academicians, and Sir Charles Blagden, who informed them that Mr Cavendish had already performed it, and that he had obtained water \*. They continued the inflammation till all their stock of gases was wasted, and obtained about 295 grains of water, which, after the most rigid examination, appeared to be perfectly pure. From this experiment Lavoisier concluded, that water is composed of oxygen and hydrogen. Mr Mongez soon after performed the same experiment, and obtained a similar result: and it was repeated again by Lavoisier and Meusnier on a scale sufficiently large to put the fact beyond doubt +.

The proof that water is a compound of oxygen and Proofs. hydrogen is, that when these two gases, mixed in proper proportions, are fired, they almost wholly disappear, and there is found in their place a quantity of pure water, as nearly equal to them in weight as can be expected in experiments of that delicate nature. The hydrogen gas is made to pass slowly from the glass jar in which it is contained, by means of a tube furnished with a stop-cock, into a glass globe filled with oxygen gas. It is set on fire at the extremity of the tube, either by means of electricity or by a little phosphorus, and it continues to burn slowly till the whole of it is consumed. New portions of oxygen gas are introduced occasionally from another glass jar, by means of a tube furnished with a stop-cock. The water, as it is formed, is condensed in the glass globe. A great num.

\* Mem. Par. 1781, p. 472. Vol. II:

+ Ibid. p. 474. E

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ber of precautions are necessary to ensure the purity of the gases, and to measure their weight and the natura of the gas which remains after combustion. But for these I refer to the account of the experiments themselves, which have been published by the French chemists in the Memoirs of the Academy of Sciences. The experiment on which the greatest dependence may be put was made in the year 1790 by Seguin, Fourcroy, and Vauquelin\*. The bulk of the gases employed in this experiment was,

> French Incher. Hydrogen gas......25980\*563 Oxygen gas.....12479\*080

The water obtained amounted to 7249.227 grains rench, or 5947.3 grains troy, or 12.390 oz. It exhibited no mark of acidity, and appeared in every respect to be pure water. Its specific gravity was to that of distilled water as 18671 to 18670; or nearly as 1.000053 to 1.

The residuum of gas in the vessel after combustion amounted to 987 cubic inches French; and, on being examined, was found to consist of the following quantities of gases:

· Sec Ann. de Gbin. viii. 230.

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51. 11.

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## WATER.

French Inches

grains less than had been employed. This approaches as near an equality as can be expected in experiments of this nature. The small surplus of azotic gas found after the combustion cannot be accounted for, unless we suppose some common air to have gained admission during the process.

As sufficient precautions had been taken to prevent the introduction of carbonic acid gas, the quantity found in the residuum must have been formed during the process. There must therefore have been a small quantity of carbon introduced. Now zinc, it is supposed, often contains carbon, and hydrogen has the property of dissolving carbon; probably, then, the carbon was introduced in this manner. The carbonic acid found in the residuum amounted to 23'306 grains, which according to Lavoisier's calculation, is composed of 8'958 grains of carbon and 14'348 grains of oxygen.

Subtracting these 8.958 grains of carbon, and the

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0.530 of a grain of hydrogen which remained in the vessel, from the total of hydrogen introduced, there will remain 852.600 grains for the hydrogen that disappeared.

Subtracting the 14.348 grains of oxygen which entered into the composition of the carbonic acid, and the residuum of oxygen, which amounted to 188.371 grains, the quantity of oxygen that disappeared will amount to 5094.6 grains.

Which is less than the gases consumed by

fire embodie seid found in

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It is impossible to account for the exact coincidence of the water condensed with the weight of the gases consumed, unless we suppose it to be composed of these bodies.

This experiment gives us the composition of water as follows :.....Oxygen...85.662 grains troy

Hydrogen 14.338

## 100.000 in air boothoatai

Dr Priestley, however, who made a great many experiments on this subject, drew from them a very different conclusion; and thought he had proved, that during the combustion the two gases combine, and that the combination is nitric acid. This theory was adopted, or rather it was suggested, by Mr Keir, who has supported it with a great deal of ingenuity \*.

Let us examine these experiments of Dr Priestley +, and see whether they warrant the conclusions he has drawn from them. The gases were exploded in vessels of copper. He found that the quantity of water obtained was alway less than that of the gases which he had used. He obtained also a considerable quantity of nitric acid. In the experiment made on the largest quantity of the gases, and from which he draws his conclusions, the quantity of liquid obtained amounted to 442 grains. This liquid was examined by Mr Keir. It was of a green colour; 72 grains of brown oxide of copper were deposited in it, and it contained a solution of nitrate of copper (copper combined with nitric acid). Mr Keir analysed this liquor : It consisted of pure water and nitrate of copper: and Mr Keir concluded that the nitric acid formed amounted to  $\frac{1}{20}$  th of the oxygen gas employed. Here then a quantity of oxygen and hydrogen gas has disappeared : What has become of them? They have combined, says Dr Priestley, and formed nitric acid. This nitric acid is only 1 th of their weight. Dr Priestley supposes, however, that it contains the whole oxygen and hydrogen that existed in these gases, and that all the rest of the weight of these gases was owing to a quantity of water which they had held in solution. Oxygen gas, then (for we shall neglect the hydrogen, which Dr Priestley was not able to bring into view at all), is composed of one part of oxygen and 19 of water. Where is the proof of this? Dr Priestley informs us, that he ascertained by experiment

\* Keir's Dictionary, art. Nitrous Acid. + Phil. Trans. #788.

composed and converted into exygen gas and hydrogen

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Book II. vision II.

that half the weight of carbonic acid gas was pure water. Supposing the experiment accurate, surely it cannot be concluded from it that oxygen gas consists of 19 parts, or almost wholly of water. It is impossible, therefore, from Dr Priestley's experiments, allowing his ingenious suppositions and conjectures their utmost force, to account for the disappearing of the two gases, or the appearance of the water, without admitting that this liquid is actually composed of oxygen and hydrogen. If we add to this, that oxygen gas can scarcely be procured absolutely free from some mixture of azote, and that his oxygen was always obtained either from red oxide of lead, or from black oxide of manganese, or red oxide of mercury, all of which substances yield a considerable proportion of azote; if we add, that it has been proved beyond the possibility of doubt, and to Dr Priestley's own satisfaction, that nitric acid is composed of oxygen and azote-we shall find it no difficult matter to explain the origin of that acid in Dr Priestley's experiments : and if we recollect that in Seguin's experiment, upon a much larger scale than Dr Priestley's, no nitric acid at all was formed, it will be impossible for us to believe that the compound formed by oxygen and hydrogen is nitric acid. Thus Dr Priestley's experiments rather confirm than destroy the theory of the composition of water. We obtain from them, however, one curious piece of information, that the presence of copper increases the quantity of nitric acid formed.

The proof for the composition of water, derived from the combustion of hydrogen gas, is rendered still stronger by reversing the experiment. When electric explosions are made to pass through water, part of it is decomposed and converted into oxygen gas and hydrogen

#### WATER.

gas. Messrs Van Troostwyck and Dieman, assisted by Chap. I. Mr Cuthbertson, filled a small glass tube,  $\frac{1}{8}$ th of an inch in diameter and 12 inches long, with distilled water. One end of this tube was sealed hermetically; but at the same time a small gold wire had been passed through it. Another wire passed through the open end of the tube, and could be fixed at greater or smaller distances from the first wire. By means of these wires, they made a great number of electrical explosions pass through the water. Bubbles of air appeared at every explosion, and collected at the top of the tube. When electric sparks were passed through this air, it exploded and disappeared almost completely. It must therefore have consisted of a mixture of oxygen and hydrogen gas, and this gas must have been formed by the decomposition of the water; for they had taken care to deprive the water beforehand of all its air, and they used every precaution to prevent the access of atmospherical air; and, besides, the quantity of gas produced did not diminish, but rather increase, by continuing to operate a number of times upon the same water, which could not have been the case had it been merely air dissolved in water : nor would atmospherical air have exploded, and left only a very small residuum, not more than "th part. They had taken care also to prove that the electric spark did not contribute to form hydrogen gas; for on passing it through sulphuric and nitric acids, the product was not hydrogen, but oxygen gas\*.

These experiments have been since repeated by Dr Pearson, assisted by Mr Cuthbertson. He produced, by means of electricity, quantities of gas from water, amounting to 56.5488 cubes of 10th of an inch each; on

\* Jour. de Phys. XXXV. 369.

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Book II. Division II. nitrons gas being added to which, it suffered a diminution of bulk, and nitrous acid appeared to have been formed. It must therefore have contained oxygen gas. When oxygen gas was added to the remainder, and an electric spark passed through it, a diminution took place precisely as when oxygen and hydrogen gas are mixed : It must therefore have contained hydrogen. When an electric spark was passed through the gas thus produced from water, the gas disappeared, being, no doubt, converted into water \*.

Such are the proofs by which the component parts of water have been ascertained. If we consider them attentively, and compare them with a vast number of other chemical phenomena, all of which tend to confirm and establish them, we must allow, I think, that scarcely any physical fact whatever can be produced, which is supported by more complete evidence. There are indeed some galvanic phenomena which scarcely seem compatible with it; but the nature of this singular power is still too imperfectly understood to warrant even a conjecture concerning it.

# II. COMBUSTIBLE OXIDES.

not have been the case had it been morely an discolved

THE oxides formed by all the simple combustibles, except hydrogen, are combustible, and of course cannot be formed by combustion. The composition of these oxides is still imperfectly known, owing to the extreme difficulty of examining them.

\* Nicholson's Jour. i. 242. These experiments are now made with great case by the galvanic apparatus.

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OXIDES OF CARBON.

I. OF CHARGOAD AND CANSONOUS ONINT

BEFORE the experiments of Morveau on the diamond

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mistake for charcoal, the substance to which he and

IT is an opinion at present pretty generally admitted by chemists, that carbon is capable of uniting with at least two doses of oxygen, and of forming two compounds, one of which is an oxide, and one an acid. The oxide is carbonic oxide, which is a combustible gas. A short sketch of the properties of this oxide has been given in a preceding part of this Work. But it will be necessary here to enter more into detail. Besides carbonic oxide, it was supposed, from the experiments of Morveau on the diamond, that there existed another oxide of carbon, containing a smaller proportion of oxygen, and that this oxide was nothing else than pure charcoal. But the late experiments of Messrs Allen and Pepys, by demonstrating the inaccuracy of Morveau's experiments, have destroyed the evidence upon which that supposition was founded. We are at present ignorant of the composition of charcoal, though it has been demonstrated that it contains at least two ingredients, carbon and hydrogen. Till the composition of this substance be better ascertained, I shall allow it to retain the place in the arrangement of chemical substances which was assigned it when it was considered as an oxide of carbon.

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## I. OF CHARCOAL AND CARBONOUS OXIDE.

BEFORE the experiments of Morveau on the diamond were made known, chemists were accustomed to confound together *carbon* and *charcoal*, though they had been carefully distinguished by Lavoisier who indeed invented the term *carbon*, to render it more difficult to mistake for charcoal, the substance to which he applied it. After these experiments became known, chemists fell into the new mistake of confounding charcoal with *carbonous oxide*, till this error was in some measure rectified by Cruickshanks and Berthollet, and till the experiments of Allen and Pepys demonstrated its, inaccuracy.

Two species of charcoal, commen 1. When charcoal is prepared in the usual way, by exposing wood in close vessels to a red heat, it always contains a portion of hydrogen: For if a quantity of this charcoal be exposed to a strong heat in a retort of porcelain, iron, or coated glass, a great quantity of gas is obtained. The gas which comes over first is a mixture of carbonic acid and heavy inflammable gas; but the proportion of carbonic acid diminishes, and at last it ceases to come over at all; yet the inflammable gas continues as copious as ever \*.

The evolution of these gases was long ascribed by chemists to the water which charcoal usually contains, and which it is known to absorb from the atmosphere with considerable avidity. If that were the case, the proportion of inflammable gas ought to diminish at the same rate with the carbonic acid; the hydrogen of the

\* Cruicksharks, Nicholson's Jonrnal, 1802, v. 219

carbon.

one being equally derived from the decomposition of Chap. I. water with the oxygen of the other. But as the evolution of inflammable gas continues after that of carbonic acid has ceased, it is scarcely possible to deny, that the hydrogen which thus escapes constituted a component part of the charcoal.

2. When common charcoal is exposed for an hour And prepain a close crucible to the strongest heat of a forge, it red. ceases to emit gas; and no temperature is sufficient to. expel gas from charcoal thus treated \*. Desormes and Clement have endeavoured to demonstrate, that by this treatment common charcoal is deprived of the whole of its hydrogen. They put a quantity of charcoal, recently exposed to the heat of a forge, and not yet cold, into the middle part of a long glass tube. To each extremity of the tube was fixed another tube, filled with dry muriate of lime, and surrounded with a mixture of snow and salt. To the extremity of one of these tubes was fixed an empty bladder; to the extremity of the other, a bladder containing a quantity of oxygen gas. The charcoal was heated to redness by placing the tube in a furnace, and then the oxygen gas was made to pass slowly over it from one bladder to the other. By this contrivance the charcoal was burnt, and converted into carbonic acid. The oxygen gas, in passing through the muriate of lime, was made to deposite the moisture which it contained, and the proportion was known by the increase of weight of the muriate. If the charcoal contained hydrogen, water would be formed during its combustion, which would unite with the

# Desprines and Clement, Ann. de Chim .xxxix. 29.

## DXIDES

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carbonic acid formed. But this gas would deposite its moisture during its passage through the muriate of lime, at the other extremity of the tube, and the increase of weight which this muriate would experience would indicate the proportion of water formed during the process. In both cases the muriate of lime was increased in weight 0.02 parts. Were we to suppose this increase owing to the formation of water, the small quantity would only contain hydrogen to the amount of  $\frac{1}{1500}$  of the charcoal; a portion too small to be regarded \*, and the propose the suppose the suppose

The same chemists tried the combustion of charcoal obtained from a variety of other substances exposed to the heat of a forge, as pitcoal, animal substances, and various wegetable substances, and found the products exactly the same. Hence they conclude that charcoal is in all cases the same, provided it be exposed to a strong enough heat. And they conclude, too, that by this strong heat the whole hydrogen of common charcoal is expelled.

But this is going rather farther than their experiments will warrant; and it is directly contrary to the experiments of Cruickshanks, who always found gases obtained by means of charcoal, in whatever state, to contain hydrogen. Besides, Berthollet has pointed out eircumstances which render the precision of these chemists somewhat doubtful.

Both contain some hydrogen. 3. Such are the facts at present known respecting the composition of charcoal. They enable us to conclude, that there are two species of charcoal, namely, common

# Ann. de Chim. xlii. 128.

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-and prepared charcoal. The first contains at least two ingredients, carbon and hydrogen; the second is deprived of a portion of its hydrogen. It consists chiefly of carbon; but it still retains a small portion of hydrogen, and is not, therefore, strictly speaking, pure carbon.

4. When the diamond is exposed to the action of heat and air, it has been observed by different experimenters to acquire a black coat not unlike charcoal. This coat may be considered as a combination of carbon and oxygen; it is perhaps carbonous oxide in a state of purity. Whether any similar combination exists native has not yet been ascertained.

## II. OF CARBONIS OXIDE.

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The substance at present known by the name of carbonic oxide, is a gas which had been confounded with carbureted hydrogen, till Dr Priestley drew the attention of chemists to it in a dissertation which he published in defence of the doctrine of phlogiston. His experiments were immediately repeated, and his opinions confirmed by Dr Woodhouse of Pennsylvania. But the real nature and composition of the gas was discovered by Mr Cruickshanks of Woolwich, and the discovery communicated to the public in 1802\*. About the time of the publication of Mr Cruickshanks' dissertation, the experiment of Woodhouse, which he had transmitted to France, engaged the attention of the National Institute. Guyton Morveau, who had been

Nicholson's Journal, V. 1. and 201.

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appointed to give a detailed account of these experiments, engaged Clement and Desormes to investigate the subject; and these gentlemen were gradually led to the same conclusions\* which had been previously drawn by Cruickshanks. The subject in the mean time attracted the attention of Bertholet, whose experiments induced him to form a different opinion respecting the composition of charcoal and carbonic oxide from that which had been entertained by the other chemists. This opinion he supported in three elaborate dissertations, published n the fourth volume of the Memoirs of the National Institute : in which he examines the experiments, and combats the conclusions of the other chemists, with his usual sagacity. About the same time a dissertation was published by the Dutch chemists, contradicting the experiments of all other philosophers, and affirming the real results to be very different +. This short historical sketch is a sufficient proof of the great difficulty attendng the investigation. No less than four different opinions have been maintained, and every one of them by men of eminence, of acknowledged skill, and undoubted candour.

Preparation, 1. There are four different processes by which carbonic oxide gas may be procured : First, When a mixture of purified charcoal and the oxides of iron or zinc, or indeed of any oxide capable of bearing a red heat, is exposed to a strong heat in an iron retort, the oxide is gradually reduced, and during the reduction a great quantity of gas is evolved. This gas is a mixture of carbonic acid gas and another which burns with a blue flame. It is to

\* Anni de Chim. III. 88. and Ili. 128.

+Ibid. zliii. #134

## OF CARBON.

this last that the term carbonic oxide has been applied. The carbonic acid may be separated by passing the gas through lime-water. Mr Cruikshanks tried in this way the oxides of iron, zinc, and copper, litharge, and the black oxide of manganese. The following conclusions result from his experiments : Those oxides which part. with their oxygen most readily yield the greatest proportion of carbonic acid; those that retain their oxygen most obstinately yield the greatest proportion of carbonic oxide. It is always towards the beginning of the process that the greatest proportion of carbonic acid gas comes over; it gradually diminishes, and at last nothing but carbonic oxide is disengaged \*. The results obtained by Clement and Desormes coincide almost exactly with the experiments of Cruikshanks. But they satisfied themselves with the white oxide of zinc, without trying those of other metals. They substituted plumbago for charcoal, and obtained the same results +.

Second, When a mixture of one part of purified charcoal, and three parts of the carbonate of lime, or of strontian, or of barytes, is exposed to a strong heat in an iron retort, the carbonic acid is gradually separated or decomposed, and gas is evolved in abundance. This gas consists of a mixture of about one part of carbonic acid to five parts of carbonic oxide ‡. In this case a portion of the carbonic acid of the carbonate is disengaged unaltered, but the greatest part of it is converted intecarbonic oxide by the action of the charcoal.

\* Nicholson's Jour. 1802, v. 2. † Ann. de. Chim. 12212. 33. ‡ Clement and Desormes, 1bid. 45. Chap. I.

Book If. Division If. Third, When a mixture of equal parts of any of the three above-mentioned earthy carbonates and clean iron filings is heated strongly in an iron retort, the carbonic acid is decomposed in like manner by the action of the iron, and the very same gases are procured in great abundance. Dr Priestley first tried this method with the black oxide of iron and carbonate of barytes; but when Cruickshanks substituted pure iron, the gaseous product was considerably increased \*.

- Fourth, When carbonic acid gas is made to pass slowly and repeatedly through prepared charcoal heated to redness in a porcelain or iron tube, it gradually disappears, and carbonic oxide is found in place of it. Here the charcoal decomposes the carbonic acid precisely as in the two last cases, with this difference only, that it is in a gaseous state, whereas in them it was combined with a base. This experiment was first made by Cruickshanks †, and afterwards by Clement and Desormes ‡.

How purified. 2. Such are the different processes for procuring carbonic oxide. From the experiments of Cruikshanks we learn, that the third method is the only one to be depended on for obtaining the gas in a state of purity. If equal parts of chalk and iron filings, previously exposed to a red heat separately in close vessels, be mixed together and strongly heated in an iron retort, the gases which come over are merely a mixture of carbonic acid and carbonic oxide; and the first being abstracted by

\* Nicholson's Jour. 1802. v. 4. and 208. † Ibid. p. 209. ‡ Ann. de Chim. xxxix+46.

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## OF CARBON.

means of lime-water, the carbonic oxide gas remains in a state of purity.

3. Carbonic oxide gas, thus obtained, is invisible and Properties, elastic like common air. Its specific gravity, according to the experiments of Cruickshanks, is 0.956, that of air being 1.000. It is to common air as 22 to 23. One hundred cubic inches of it weigh 30 grains. The result obtained by Desormes and Clement does not differ much from this \*.

Animals cannot breathe this gas without suffocation. Birds put into it by Desormes and Clement dropt down dead before they had time to take them out; and when they attempted to breathe it themselves, the consequence was giddiness and faintness +. Neither will any combustible body burn in it.

It is not altered by exposure to light, nor by passing it through a red hot tube. From the experiments of Clement and Desormes, we find that it is dilated by heat exactly like common air, as was indeed to be expected.

4. Carbonic oxide gas is combustible. It takes fire Combustiin the open air when it comes in contact with a red hot body, or when it is presented to the flame of a candle. and burns with a lambent blue flame. When mixed with common air before it is kindled, it burns more rapidly and brilliantly, but does not detonate. The com-

\* Bytaking a mean of their experiments, we obtain the weight of a litre of gas 1.135 grammes, which reduced to our standard gives the weight of 100 cubic inches 28.7 grains. Their result would have been still nearer Cruikshanks', had I excluded their trials with some of the lightest and impurest gases which they obtained.

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† Ann. de Chim. XXXIX. 56.

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Book II. Division II. bustion is still more rapid and brilliant if we substitute oxygen gas for common air. Sometimes it detonates with oxygen, but most commonly the detonation does not take place.

From the experiments of Cruickshanks, which have been confirmed by those of Clement and Desormes, we learn that 100 cubic inches of carbonic oxide, in order to undergo complete decomposition, must be mixed before combustion with 40 cubic inches of oxygen gas; and this mixture, being exploded by electricity in a detonating tube, is converted into 92 cubic inches of carbonic acid gas. Or, in numbers, 30 grains of carbonic exide require for saturation about 13.6 grains of oxygen; and the resulting compound amounts to 43.6 grains of carbonic acid gas. No sensible quantity of water is formed by the combustion of this gas when it is procured by the third process, and made as dry and pure as possible before the experiment.

Action of simple combustibles. 5. This gas has no action whatever upon the simple combustibles at the common temperature of the atmosphere; but its activity is somewhat augmented by the assistance of heat.

When passed through melted sulphur, it does not combine with it, nor alter its properties; but it dissolves a little phosphorus, and acquires the property of burning with a yellow flame. When passed through red hot charcoal, it dissolves a part of it, if we believe Desormes and Clement, and its specific gravity is increased. The same chemists affirmed, that when a mixture of carbonic oxide and hydrogen gas is made to pass through a red hot glass tube, charcoal is deposited, which lines the inside of the tube with a shining enamel; that water is formed, and hydrogen, seemingly pure,

## OF CARBON.

disengaged from the other end of the tube \*. But when this experiment was repeated by Saussure junior, he found that the supposed enamel of charcoal was merely the black (or rather bluish) colour which flint glass acquires when hydrogen is brought in contact with it at ared heat, as had been previously observed by Dr Priestley ‡. Indeed it is very unlikely that hydrogen gas is capable of decomposing carbonic oxide ; as Saussure has shown, that when carbonic acid and hydrogen gas are made to pass through a red hot tube, the acid is decomposed, and carbonic oxide produced—a result which has been even confirmed by the subsequent experiments of Clement and Desormes.

6. None of the simple incombustibles produce any change upon carbonic oxide at any temperature hitherto tried; but the action of oxymuriatic acid gas upon it is extremely curious and important. For the investigation of this part of the subject we are entirely indebted to Mr Cruikshanks, who has thereby disclosed to chemists a new and valuable method of trying the purity and composition of the combustible gases.

If a phial be filled with a mixture of two measures of carbonic oxide gas and  $2\frac{\pi}{5}$  measures of oxymuriatic acid gas  $\ddagger$ , then closed with a ground stopper, and allowed to remain for 24 hours with its mouth inverted under mercury, on drawing the stopper under water, two-thirds of the gas are immediately absorbed, and all the rest by agitation in lime-water (except  $\frac{\pi}{5}$ th of a

Of incombustibles,

Of oxymuriatic acid.

\* Ann. de Chim. xxxix. 61. + Jour. de Phys. 1v. 396. † Procured by pouring mutiatic acid on the hyperoxymuriate of potash.

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measure of azote)\*. Hence we see that these two gases act upon each other at the temperature of the atmosphere; that the carbonic oxide gradually abstracts oxygen from the other gas, and is converted into carbonic acid. The oxymuriatic gas thus decomposed is converted into muriatic acid, which is instantly absorbed on the admission of water. Thus by the mutual action of the two gases, the whole is converted into carbonic acid and muriatic acid.

Mr Cruikshanks ascertained that this mixture of carbonic oxide and oxymuriatic acid gas does not burn when electric sparks are made to pass through it, nor is its nature altered; whereas a mixture of carbureted hydrogen and oxymuriatic acid gas explodes immediately. This difference enables us to distinguish carbureted hydrogen from carbonic oxide with the greatest facility  $\ddagger$ .

Of metals,

7. From any experiments hitherto made, it does not appear that carbonic oxide is capable of acting on the metals; but Clement and Desormes affirm, that when passed hot over the red oxide of mercury, it produces a commencement of reduction. Indeed it is very likely that it will be found capable of reducing several of the metallic oxides, especially those that part with their oxygen easily.

Alkalies and earths. 8. Neither the fixed alkalies nor the earths have any action on carbonic oxide. Neither does ammonia alter it when passed with it in the state of gas through a red hot tube  $\ddagger$ .

\* Nicholson's Journal, 1802, v. p. 205.

+ Ibid. p. 207 ...

t Clement and Desormes, Ann. de Chim. xxxix. 61.

## OF CARBON.

9. From the history of the properties of this gas just given, it must be obvious at once, that it contains carbon as an ingredient; for when fired with oxygen, it yields carbonic acid gas as a product. That it differs from carbureted hydrogen is obvious from its specific gravity, from the action of oxymuriatic acid gas, and from the result obtained by burning it. As it yields on combustion no perceptible portion of water, it was concluded by Cruikshanks, and afterwards by Guyton Morveau, Desormes and Clement, that it contained no hydrogen, and contained no other combustible base besides carbon. But it requires much less oxygen gas for combustion than charcoal. Thus 100 parts of charcoal require 257 parts of oxygen to saturate them; whereas 100 parts of carbonic oxide require only  $45\frac{1}{3}$ parts of oxygen; and in both cases carbonic acid is pro-This remarkable difference can only be acduced. counted for by supposing that the carbonic oxide is already combined with a portion of oxygen, and therefore a smaller addition must be sufficient to saturate it. Accordingly this was the consequence drawn by Cruikshanks; and it is impossible to resist the evidence in favour of his conclusions. The gas therefore, according to this reasoning, is a compound of carbon and oxygen. Hence the name carbonic oxide given to it by chemists.

If we suppose, according to the experiments of Lavoisier, that carbonic acid is composed of 28 carbon and 72 oxygen, and consider the experiments of Cruikshanks as approaching to accuracy, it will be easy for us to ascertain the component parts of this oxide.

According to Cruikshanks, 30 grains of carbonic oxide combine by combustion with about 13.6 grains of 140

Chap. I. Composition.

Book II. oxygen, and the carbonic acid formed amounts to a-Division II. bout 43.6 grains. Hence it follows, that carbonic acid is composed of about and a manbergor by 25 not

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## from the result obtained by 5.001 and But 100 carbonic acid are composed of 72 exygen and

eravity, from the solice of oxymuniatic acid get, and

28 carbon. We have therefore this equation, Carbon, Oxygen, Carb.Ox. Oxygen,

28 + 72 = 69 + 31

Carbon, Oxygen. Carb. Oxide.

$$28 + 41 = 69$$

That is to say, 69 parts of carbonic oxide are composed of 28 parts of carbon and 41 of oxygen. course we have per cent, about 41 carbon at bits asyvice to strang

59 oxygen counted for by supposing that the

## 100 carbonic oxide

And 100 parts of carbon united to 146 of oxygen form 246 of carbonic oxide. Accordingly this was the cor

But all this statement has been called in question by Berthollet, According to this sagacious philosopher, there are two different species of inflammable gases containing carbon. The first species is composed of carbon and hydrogen ; the second, of carbon, hydrogen, and oxygen. To distinguish these two species from each other, he calls the first carbureted hydrogen; the second oxycarburcted bydragen. To the first species belong the gases obtained by passing alcohol through a red hot tube, by distilling oil, and by exposing moist charcoal to a red heat, &c. To the second species belong the gas produced by exposing charcoal to a strong

Theory of Bertholler.

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## OF CARBON.

heat, the gas obtained by distilling sugar, the gas described in this Section under the name of carbonic oxide, &c. There are many varieties of these gases, differing from each other in the proportions of their ingredients : and the gases belonging to the first species may, by various processes, be converted into the second. He calculates the proportion of hydrogen in carbonic oxide to be about  $\frac{1}{25}$  th of the whole.

These conclusions are obviously irreconcileable with the experiments of Cruikshanks and of Desormes and Clement, and cannot therefore be admitted without very decisive proofs. The carbonic oxide obtained by Cruikshanks, when as pure as possible, yielded no perceptible quantity of water when burnt with oxygen. But Berthollet observes that all gases contain water as a constituent part, and shows that all the water that could have been formed would have combined with the carbonic acid gas, and remained invisible. Even if we were to grant this, and to allow that some water has been formed in every case of the combustion of carbonic oxide with oxygen hitherto tried, still Mr Berthollet's hypothesis would stand upon as weak ground as ever. For it is obvious from the experiments of Cruikshanks, that the drier he made his materials the purer was the gas, or the less water was formed during its combustion; and when he employed bodies that could not contain any hydrogen except in the state of water (namely, dry chalk and tin or iron), the gas was obtained purest of all.

Mr Berthollet's chief reason for affirming that carbonic oxide must contain hydrogen is its small specific gravity. The specific gravity of

oxygen gas is 1.103

Chap. J.

## carbonic oxide 0.956 carbonic acid 1.500

The specific gravity of carbon is undoubtedly much greater than any of the three. Now when oxygen gas combines with carbon, and forms carbonic acid, its specific gravity is increased, as happens in other cases. But how is it possible, says Berthollet, to conceive that the addition of carbon should diminish the specific gravity of oxygen gas, as would be the case if carbonic oxide were composed of these two ingredients only? Nay, carbonic acid, by dissolving an additional dose of carbon, would not only become specifically lighter than before, but even specifically lighter than oxygen gas, which Berthollet considers as incredible. But this reasoning is by no means sufficient to induce us to refuse credit to the conclusions of Cruikshanks; for similar instances are by no means so uncommon as Berthollet supposes. Mr Davy has given us an example which has some analogy to the case under our consideration \*. The specific gravity of oxygen gas is 1.103

azotic gas 0.985 nitrous oxide 1.603 nitric oxide 1.094

Now when nitric oxide is converted into nitrous oxide by abstracting a portion of its oxygen, the heaviest of its component parts, its specific gravity is increased. This is as great an anomaly as that at which Mr Berthollet startles.

\* Journals of the Royal Institution, i. 317.

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## OF SULPHUR AND PHOSPHORUS.

SECT. III.

## OXIDES OF SULPHUR AND PHOSPHORUS.

WE ought now to proceed to the consideration of the oxides of sulphur and phosphorus, which constitute the remainder of the oxide supporters; but these bodies are still too imperfectly known to admit of a separate discussion. The small number of facts which have been ascertained were detailed in the first Book of this Work, while the substances themselves, which constitute the bases of these oxides, were under examination.

## **III. OXIDE SUPPORTERS**

THE oxides whose bases are the simple incombustibles cannot be formed by combustion, but make their appearance in processes nearly the reverse of combustion; and hence it happens that the oxygen which they contain is still capable of supporting combustion. Chemists have given the name of oxide to those oxides only whose base is azote; the oxide of muriatic acid has been considered as an acid. This will prevent us from taking it into consideration in this Chapter; but a sketch of some of its most important properties was given when we were treating of its base. 153

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## SECT. IV.

## OF THE OXIDES OF AZOTE.

AZOTE and oxygen form two different oxides, both of which were discovered by Dr Priestley. They can only be exhibited in the state of a gas: Hence the first of them has been called *nitrous oxide gas*; the second, *nitric oxide gas*.

## I. NITROUS OXIDE GAS.

History,

NITROUS oxide gas was discovered by Dr Priestley about the year 1776, and called by him *dephlogisticated nitrous gas*. The associated Dutch chemists examined it in 1793, and demonstrated it to be a compound of azote and oxygen\*. But for a full investigation of its properties we are indebted to Mr Davy, who published an excellent dissertation on it in the year 1800. He gave it the name of *nitrous oxide*<sup>+</sup>.

Preparation. 1. It may be procured by the following process: Take any quantity of *nitrate of ammonia* (a salt composed of nitric acid and ammonia) in crystals, and expose it in a retort, by means of a lamp, to a heat not under 340°, nor above 500°. It melts rapidly, and is decomposed, emitting a great quantity of gas, which is-

\* Jour. de Pbys. xlii. 323.

+ Researches, chiefly concerning Nitrous Oxide.

sues from the mouth of the retort, and may be received in glass jars in the usual manner. The gas which comes over is nitrous oxide. This process was first pointed out by Berthollet; but it was much simplified 

2. Nitrous oxide gas, thus obtained, has all the me- Properties. chanical properties of air : but it is much heavier than air ; its specific gravity, according to Davy, is 1.603, that of air being 1.000. It is to common air nearly as 5 to 3 7. One hundred cubic inches of it, at the temperature of 60°, barometer at 30 inches, weigh 49.706 grains. Ind awo an yimoa confer to publicate to very

It is capable of supporting combustion even better than common air; almost as well indeed as oxygen gas. A candle burns in it with a brilliant flame and a crackling noise. No combustible, however, burns in it, unless it be previously brought to a state of ignition.

Dr Priestley and the Dutch chemists had concluded that it cannot be respired ; but they did not examine it in a state of purity ‡. Mr Davy ascertained that it may be breathed for several minutes without any bad effects. The feelings produced by breathing it bear a strong resemblance to intoxication; but they are not followed by that langour and debility which is a con-

\* Mr Proust has remarked, very justly, that the gas which comes over at the beginning of the process differs a little from nitrous oxide, and yet it is not nitrous gas.

+ Davy's Researches, p. 94.

t Dr Priestley indeed found, in one instance, that a mouse breathed it five minutes without uncasiness. In this experiment he seems to have obtained it nearly pure .- Priestley, ii, 84,

Chap. J.

JUSTICS!

Book II. Division II. stant attendant of intoxication \*. It cannot be breathed longer than about four minutes, without the loss of voluntary motion altogether. When animals are confined in it, they give no signs of uneasiness for some moments; but they soon became restless, and, if not removed in a very few minutes, die altogether. Hence we see that, though this gas be respirable, it is much less so than common air or oxygen gas ‡.

Action of water. 3. This gaseous oxide is absorbed pretty rapidly by water, as Dr Priestley ascertained, especially when agitated. Water absorbs 0.86 parts of its bulk of this gas, or according to Dalton nearly its own bulk of it. It acquires a sweetish taste; but its other properties do not differ perceptibly from common water. The whole of the gas is expelled unaltered by boiling the water  $\ddagger$ .

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\* Mr Davy describes the effects it had upon him as follows : "Having previously closed my nostrils and exhausted my lungs, I breathed four quarts of nitrous oxide from and into a silk bag. The first feelings were similar to those produced in the last experiment (giddiness); but in less than half a minute, the respiration being continued, they diminished gradually, and were succeeded by sensations analogous to gentle pressure on all the muscles, attended by an highly pleasureable thrilling, particularly in the chest and the extremities. The objects around me became dazzling, and my hearing more acute. Towards the last inspirations, the thrilling increased, the sense of muscular power became greater, and at last an irresistible propensity to action was indulged in; I recollect but indistinctly what followed; I know that my notions were various and violent.

"These effects very soon ceased after respiration. In ten minutes I had recovered my natural state of mind. The thrilling in the extremities continued longer than the other sensations." Davy's *Researches*, p. 457. The gas has been breathed by a very great number of persons, and almost every one has observed the same things. On some few, indeed, it has no effects whatever, and on others the effects are always painful.

+ Davy's Researches, p. 94. ‡ Priestley, ii. 81.

When this gas combines with the water, it expels the common air which was formerly dissolved in the water. Hence the residuum of common air, which always appears when this gaseous oxide is exposed to a sufficient quantity of water \*.

4. This gas is not altered by exposure to light, nor to any heat below ignition; but when made to pass through a red-hot porcelain tube, or when electric sparks are made to traverse this gas, it is decomposed, and converted into *nitric acid* and *common air* †.

5. There is no action between this gas and air or oxygen gas.

6. Sulphur, at the common temperature of the air, is not altered by this gas. If it be introduced into it while burning with a blue flame, it is immediately extinguished; but if introduced while burning with a white flame, it continues to burn for some time with great brilliancy, and with a fine red flame. The products are sulphuric acid and azote. When about the half of the nitrous oxide is decomposed, the sulphur is extinguished ‡.

Phosphorus may be melted and sublimed in this gas without alteration; it may be even touched with a red hot wire without undergoing combustion; but when touched with a wire heated to whiteness, it burns, or rather detonates, with prodigious violence. The products are, azotic gas, phosphoric acid, and nitric acid: a part of the oxide remains undecomposed ||.

Charcoal, confined in this gaseous oxide, may be kindled by means of a burning-glass. It continues to

Davy, p. 89.
 Priestley, ii. 91. and Davy, ibid. p. 279 Davy, ibid. p. 303.
 Ibid.

Of the simple combustibles.

Chap. T.

Book II. Division II. burn with great brilliancy, till about the half of the gas is consumed. The products are carbonic acid gas and azotic gas \*.

Hydrogen gas and nitrous oxide gas detonate violently with a red flame, when a strong red heat is applied, or when the electric spark is made to pass through the mixture. When the proportion of hydrogen is nearly equal to that of the oxide, the products are water and azote; when the proportion of hydrogen is small, nitrie acid is also formed  $\ddagger$ .

Sulphureted, phosphureted, and carbureted hydrogen gas, likewise burn when mixed with nitrous oxide, and exposed to a strong red heat. The products differ according to the proportions of the gases mixed.

7. Neither azote nor muriatic acid appear to have any marked action on this gaseous oxide.

Of the me-

8. On some of the metals it acts with great energy at high temperatures. Thus iron wire burns in it with the same brilliancy as in oxygen gas, though the combustion lasts but a very short time. The iron is converted into black oxide; part of the nitrous oxide is decomposed, its azote is evolved, while its oxygen combines with the iron ‡. Zinc also may be oxidized in this gas §. Its effect upon the other metals has not been tried.

Azotites.

9. Oxide of azote is capable of combining with alkalies, and forming salts of a very peculiar nature; for the discovery of which we are indebted to the sagacity of .Mr Davy. No combination takes place when the alka-

\* Davy, p. 311, ‡ Ibid. ii. 86. + Priestley, ii. 83. and Davy, p. 286. § Davy, p. 317.

## OF AZOTE.

lies are exposed to nitrous oxide in the gaseous state. But if it come into contact with them at the instant of its formation, it combines with them very readily. As these combinations have not yet received a name, we may call them *azotites* till some better appellation be thought of \*.

Azotite of potash may be formed by the following process: Nitrous gas (a substance which will be described immediately), by confining in it crystallized sulphite of potash<sup>+</sup>, is gradually deprived of a portion of its oxygen, and converted into nitrous oxide. If very finely pulverised sulphite of potash, mixed with potash, be exposed for a great length of time in a sufficient quantity of nitrous gas, it is changed almost completely into sulphate of potash, while the oxide of azote, as it is evolved, combines with the pure potash. Consequently the salt is converted into a mixture of sulphate of potash and azotite of potash. The sulphate may be separated by solution, evaporation, and crystallization in a low temperature.

Azotite of potash is obtained in irregular crystals. It is composed of about three parts of alkali and one part of nitrous oxide. It is soluble in water. Its taste is caustic, and it has a peculiar pangeney. It converts vegetable blues into green. Pulverised charcoal, mix-

\* Mr Davy has proposed to call them *nitraxis*; but this name is exceptionable, not only because it is contrary to the idiom of the English language, but because it is inconsistent with the rules laid down for forming chemical terms.

+ Potash combined with sulphurous acid. This salt has a strong affinity for oxygen. It absorbs it from nitrous gas, and is converted intesulphate of potash. Hence the change of nitrous gas to nitrous oride. 150

Chap. I.

Book II. Division II. ed with it, and inflamed, burns with slight scintillations. When projected into zinc in fusion, a slight inflammation takes place. All acids, even carbonic, seem capable of expelling the nitrous oxide from the potash\*. The other properties of this salt have not been examined.

Azotite of soda may be formed in the same manner. and seems to agree nearly in its properties with azotite of potash. The nitrous oxide is disengaged from it by a heat of between 400° and 500°. Its taste is more acrid than that of azotite of potash, and it seems to contain less oxide of azote +.-

Mr Davy did not succeed in combining nitrous oxide with ammonia and earths; but he has rendered it probable that these azotites may be formed.

Composition.

10. From the history of the properties of nitrous oxide gas just detailed, it is obvious that it is a supporter of combustion, and therefore that it contains oxygen in the same state as it exists in other supporters. That its other component part is azote, cannot be doubted, if we consider that either azote or nitric acid is constantly evolved when nitrous oxide is decomposed. The experiments of Mr Davy leave no doubt that these two substances are its only constituents. This philosopher found that 39 measures of nitrous oxide gas are capable of saturating 40 measures of hydrogen, and that after combustion the residue consists of 41 measures of azotic gas. But 40 measures of hydrogen were found to require 20.8 measures of oxygen 1. From this it follows, that

\* Davy, p. 362. 1 Ibid. p. 291.

in a straight of the state of the state of the + Ibid. p. 268.

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if the component part of nitrous oxide were merely mixed together, the bulk of them would occupy a third more room than when combined; for 40 measures of nitrous oxide would be resolved into 20.8 measures of oxygen gas and 40 measures of azotic gas \*: But 20.8 cubic inches of oxygen gas weigh about seven grains, and 40 of azotic gas about 12 grains. Hence it follows, that nitrous oxide is composed of seven parts by weight of oxygen, and 12 of azote, or nearly

> 63 azote, 37 oxygen;

> > 100

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This statement coincides very nearly with the specific gravity of nitrous oxide. Thirty-nine cubic inches of nitrous gas, if the composition-here given were precise, ought to weigh 19.38 grains. In reality they weigh 19.69 grains. The component parts of this gas, as obtained by the Dutch chemists, differ very little from the result of Mr Davy's experiments.

Much is still wanting to render the history of this singular substance complete. Mr Davy has laid open a very interesting field of investigation, which promises, if pursued far enough, to throw much light upon the nature of combustion: an operation more intimately connected with azote and its compounds than is at present supposed.

\* I omit one measure, because the gases were not absolutely pure. Vol. II.

in succession

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Book II. Division II.

## II. NITRIC OXIDE.

more room than when combined : fir 40 mes.

History.

NITRIC OXIDE, usually denominated *nitrous gas*, was obtained accidentally by Dr Hales; but its nature and properties were investigated by Priestley, in one of the first excursions made by that illustrious philosopher into the then unbeaten tracts of pneumatic chemistry. As the phenomena exhibited by this oxide are intimately connected with the most important investigations in chemistry, its properties were examined with great care, and occupied the attention of almost every chemist of eminence.

Preparation. 1. It may be obtained by the following process: Put copper or mercury into a glass retort, and pour over it somewhat diluted nitric acid. The metal is rapidly dissolved with a strong effervescence, and a great quantity of gas issues from the mouth of the retort, which may be received in glass jars. This gas is *nitrous gas*.

Properties.

2. When pure it is invisible like common air, of which it possesses the mechanical properties. Its specific gravity is 1.094, that of air being 1.000, according to Davy \*. Nitrous gas, then, is to common air nearly as 34 to 31. One hundred cubic inches of it, at the temperature of 60°, barometer 30 inches, weigh 33.923 grains.

Nitrous gas is exceedingly noxious to animals, producing instant suffocation whenever they attempt to breathe it.

\* Researches, p. 6,

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## OF AZOTE.

The greater number of combustible bodies refuse to burn in it: A taper, for instance, is extinguished the moment it is plunged into nitrous gas; the same thing happens to sulphur, even though previously burning with a white flame. It is capable, however, of supporting the combustion of several bodies, as has been ascertained by the experiments of Priestley and Davy. When Homberg's pyrophorus \* is introduced into nitrous gas, it takes fire spontaneously, just as it does in common air. Phosphorus, too, when introduced into this gas in a state of inflammation, burns with as much splendour as in oxygen gas †.

4. When nitrous gas and common air are mixed together, the mixture instantly assumes a yellow colour, heat is evolved, and the bulk of the two gases diminishes considerably; slowly, if the experiment be made over mercury; but rapidly, if it be made over water. When the diminution has reached its maximum, the mixture becomes perfectly transparent. The yellow colour is owing to a quantity of nitrous acid which is formed, and the diminution of bulk to the gradual absorption and condensation of this acid. What remains after this absorption is only azotic gas. The cause of this remarkable phenomenon is obvious. The nitrous gas combines with the oxygen of the air, and forms nitrous acid which is condensed ; while the azote of the air remains behind in the form of a gas. Hence with equal quantities of nitrous gas and air the diminution of bulk is always proportional to the quantity of

\* This substance will be described hereafter. The combustible part of it is charcoal and subshar.

+ Davy, p. 134.

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Chap. I. Supports combustion.

Action of air.

Absorbed by water.

Action of

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| Priceley, il. 40%.

Book II. Division II. And oxygen.

oxygen present in the air. Hence it informs us of the proportion of that substance in any particular air. The same phenomenon takes place when oxygen gas and nitrous gas are mixed; but the condensation is much more considerable. Indeed it would be complete, provided the two gases were perfectly pure, and mixed in the proper proportions.

From the experiments of Mr Dalton we learn that nitrous gas combines with two different proportions of oxygen gas. 21 measures of oxygen gas uniting either with 36 measures of nitrous gas, or with 72 measures\*.

When electric sparks are made to pass through nitrous gas, it is decomposed and converted into nitrous acid and azotic gas +.

Absorbed by water.

fo colto

5. Nitrous gas is readily absorbed by water. From an experiment of Mr Davy, it appears that 100 cubic inches of water at the common temperature, and previously freed from air, absorb 11.8 cubic inches of nitrous gas, or nearly one-tenth, as Dr Priestley had ascertained; but the experiments of Dr Henry do not accord with this estimate. Water, by his trials, at the temperature of 60°, absorbs only five *per cent*. of its bulk of this gas ‡. This solution has no particular taste, and does not redden blue vegetable colours. The gas is expelled again by boiling the water §; it separates likewise when the water is frozen ||.

Action of combustibles, 6. Nitrous gas is decomposed by phosphorus and charcoal at a very high temperature, and probably also

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## DF AZOTE.

by sulphur. These substances are converted into acids by combining with the oxygen of the gas while its azote is evolved.

Hydrogen gas mixed with it acquires the property of burning with a green flame. A mixture of these two gases does not take fire when electric sparks are made to pass through it; but according to Fourcroy, it detonates when made to pass through a red hot porcelain tube; water is formed, and azotic gas is evolved \*.

7. Nitrous gas has no action whatever on azotic gas, Incombuseven when assisted by heat. Neither does it act on muriatic acid.

8. Several of the metals have the property of decom- Andmetals. posing it, especially when assisted by heat. This is the case particularly with iron. Dr Priestley confined a portion of nitrous gas for some time in contact with a number of iron nails; the gas was converted into oxide of azote, in consequence, doubtless, of the iron ab-, stracting part of its oxygen +. It was in this manner that nitrous oxide was discovered by that philosopher. When the iron is heated to redness by means of a burning-glass, the decomposition is complete, the whole of the oxygen is abstracted from the nitrous gas, and only azotic gas remains behind 1.

9. Dr Priestley ascertained that nitrous gas is absorbed by the green sulphate of iron; a property which is employed successfully to ascertain its purity. All that is necessary is, to expose a given portion of nitrous gas in a close vessel to the action of the green sulphate;

Absorbed by sulphate of iron.

tibles,

\* Fourcroy, ii. 91. ‡ Ibid. p. 38.

+ Priestley, ii. 54.

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Chap. I.

Book II. Division II. the quantity of gas which remains unabsorbed gives the proportion of foreign bodies with which it is mixed. Mr Davy has proved, that all the salts containing the black oxide of iron possess the same property, and that they all absorb nitrous gas unaltered. The greatest part of it may even be expelled again by the application of heat. Several other metallic salts possess the same properties \*.

Converted into nitrous oxide. 10. The following bodies have the property of converting nitric oxide into nitrous oxide.

> Alkaline sulphites, Hydrogureted sulphurets, Muriate of tin, Sulphureted hydrogen gas, Iron or zinc filings moistened with water.

- Lord beteinen noten nove

To produce this effect, nothing more is necessary than to put these substances into jars filled with nitric oxide gas, and allow them to remain for a week or two. The substances gradually combine with a portion of oxygen, and are converted into oxides or salts  $\dagger$ .

11. Nitrons gas is absorbed by alkaline solutions; but it does not appear from the experiments hitherto made, that it is capable, like oxide of azote, of combining with alkalies and earths, and forming salts.

Composi-

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12. The conversion of nitric oxide gas into nitric acid, by combining it with oxygen, is a demonstration that it

\* Davy, p. 179.

† Priestley and Davy, *possim.*—During the action of the two last bodies on nitrous gas, ammonia is likewise formed.

#### OF AZOTE.

contains azote as a constituent part; and the property which several bodies have of absorbing oxygen from it, and converting it into nitrous oxide gas, is a demonstration that oxygen is the only other ingredient which it contains. But it is by no means easy to ascertain the proportion of these two constituents. Mr Lavoisier, from a set of experiments made at an early period, and in a manner not susceptible of much accuracy, estimated their proportions at about 68 oxygen and 32 azote. But this estimate is irreconcileable with the experiments of other philosophers. The proportions obtained by Mr Davy deserve much more confidence, as his method was susceptible of greater accuracy. By means of a burning-glass he exposed to the action of the sun's rays a small portion of prepared charcoal, placed in a measured quantity of nitric oxide gas standing over mercury. The weight of the charcoal did not exceed a quarter of a grain, and the gas amounted to 16 very small measures. After the process was finished, the bulk of the gas was increased about 3ths of a measure. The whole of the nitric oxide was decomposed. Potash ley rapidly absorbed the whole of the gas except eight measures, which were pure azote. But the gas originally was found by experiment to contain 0.6 of a measure of azote. Therefore 15.4 measures of nitric oxide, when decomposed by charcoal, are converted into 16.15 measures ; 7.4 of which are azote, and 8.75 carbonic acid. But 15.4 measures of nitric oxide weigh 5.2 grains, and 7.4 measures of azote weigh 2.2 grains. Hence it follows that 5.2 grains of nitric oxide contain 2.2 of azote; the remaining 3 grains must be oxygen. This gives us nitric oxide composed of 2.2 azote and 3 oxygen, or of 57.7 oxy167

Chap. I.

Book II. Division II. gen and 42.3 of azote. The carbonic acid produced weighed 4.1 grains, and contained 1.15 grains of charcoal combined with 2.95 grains of oxygen, which it had absorbed from the nitric oxide. This gives us 5.2 grains of nitric oxide, composed of 2.95 oxygen and 2.25 azote; or 100 parts contain 57 oxygen and 43 azote, which differs very little from the last estimate \*. We may consider the last numbers as the nearest approximations to the composition of nitric oxide.

The proportion of oxygen contained in the compounds of azote, according to these results, may there, fore be stated thus:

Azote.	Oxygen.	- states and
100	58.7	Nitrous oxide
100	136	Nitric oxide
100	236	Nitric acid

Hence it follows that

 Nitrous
 Nitric
 Nitric

 1.00 + 0.58 = 1.58 0xygen.
 oxide.
 Nitric

 1.58 + 0.78 = 2.36 0xygen.
 acid.

 2.36 + 1.00 = 3.36

\* Davy, p. 129.

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ACIDS.

# CHAP. II.

## OF ACIDS.

THE word ACID, originally synonymous with Sour, and applied only to bodies distinguished by that taste, has been gradually extended in its signification by chemists, and now comprehends under it all substances possessed of the following properties :

1. When applied to the tongue, they excite that sensation which is called *sour* or *acid*.

2. They change the blue colours of vegetables to a red. The vegetable blues employed for this purpose are generally infusion of litmus and syrup of violets or of raddishes, which have obtained the name of *reagents* or *tests*. If these colours have been previously converted to a green by alkalies, the acids restore them again.

3. They unite with water in almost any proportion.

4. They combine with all the alkalies, and most of the metallic oxides and earths, and form with them those compounds which are called *salts*.

It must be remarked, however, that every acid does

Properties.

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Chap. II.

#### PRIMARY COMPOUNDS.

Book II. Division II. not possess all these properties; but all of them possess a sufficient number of them to distinguish them from other substances. And this is the only purpose which artificial definition is meant to answer.

The acids are by far the most important class of bodies in chemistry. It was by their means indeed, by studying their properties, and by employing them as instruments in the examination of other bodies, that men of science laid the foundation of chemistry, and brought it to that state in which we find it at present. The nature and composition of acids, therefore, became a very important point of discussion, and occupied the attention of the most eminent cultivators of the science.

Opinion concerning the acid principle.

Paracelsus believed that there was only one acid principle in nature which communicated taste and solubility to the bodies in which it was combined. Beccher embraced the same opinion ; and added to it, that this acid principle was a compound of earth and water, which he considered as two elements. Stahl adopted the theory of Beccher, and endeavoured to prove that his acid principle is sulphuric acid; of which, according to him, all the other acids are mere compounds. But his proofs were only conjectures or vague experiments, from which nothing could be deduced. Nevertheless, his opinion. like every other which he advanced in chemistry, continued to have supporters for a long time, and was even countenanced by Macquer. At last its defects began to be perceived : Bergman and Scheele declared openly against it; and their discoveries, together with those of Lavoisier, demonstrated the falsehood of both parts of the theory, by showing that sulphuric acid does not with bloss where and the areas of the second deal data

#### ACIDS.

exist in the other acids, and that it is not composed of Chap. II. water and earth, but of sulphur and oxygen.

The opinion, however, that acidity is owing to some principle common to all the salts, was not abandoned. Wallerius, Meyer, and Sage, had advanced different theories in succession about the nature of this principle; but as they were founded rather on conjecture and analogy than direct proof, they obtained but few advocates. At last Mr Lavoisier, by a number of ingenious and accurate experiments, proved that several combustible substances when united with oxygen form Supposed acids; that a great number of acids contain oxygen; and that when this principle is separated from them, they lose their acid properties. He concluded, therefore, that the acidifying principle is oxygen, and that acids are nothing else but combustible substances combined with oxygen, and differing from one another according to the nature of the combustible base.

This conclusion, as far as regards the greater number of acids, is certainly true. All the simple combustibles, except hydrogen, are convertible into acids; and these acids are composed of oxygen and the combustible body combined. This is the case also with four of the metals. It must not, however, be admitted without some limitation.

1. When it is said that oxygen is the acidifying principle, it is not meant surely to affirm that oxygen possesses the properties of an acid, which would be contrary to truth; all that can be meant is, that it enters as a component part into acids, or that acids contain it as an essential ingredient.

2. But, even in this sense, the assertion cannot be admitted as demonstrated. For it has not yet been shown 171

oxygen.

#### FRIMARY COMPOUNDS.

Book II. Division II. that oxygen is an essential ingredient in all acids. Muriatic acid, for example, has not yet been proved to contain oxygen, and the same observation applies to some other substances universally admitted among acids.

3. When it is said that oxygen is the acidifying principle, it cannot be meant surely to affirm that the combination of oxygen with bodies produces in all cases an acid, or that whenever a body is combined with oxygen, the product is an acid; for the contrary is known to every chemist. Hydrogen, for instance, when combined with oxygen, forms not an acid, but water, and the greater number of metallic bodies form only oxides.

The recent discoveries of Mr Davy render this, if possible, still more obvious. For we now know that the alkalies contain oxygen, and that they are as much indebted to that principle for their alkaline qualities as the acids are to it for their acid qualities.

All that can be meant, then, when it is said that oxygen is the acidifying principle, is merely that it exists as a component part in the greater number of acids; and that many acids are formed by combustion, or by some equivalent process. The truth is, that the class of acids is altogether arbitrary; formed when the greater number of the bodies arranged under it were unknown, and before any precise notion of what ought to constitute the characteristic marks of an acid had been thought of. New bodies, when they were discovered, if they possessed any properties analagous to the known acids, were referred without scruple to the same class, how much soever they differed from them in other particulars. Hence we find, under the head of acids, bodies which have scarcely a single property in com-

mon except that of combining with alkalies and earths. Chap. II. What substances, for instance, can be more dissimilar than sulphuric, prussic, and uric acids? Hence the difficulty of assigning the general characters of the class of acids, and the disputes which have arisen about the propriety of classing certain bodies among acids. If we lay it down as an axiom that oxygen is the acidifying principle, we must either include among acids a great number of bodies which have not the smallest resemblance to those substances which are at present reckoned acids, or exclude from the class several bodies which have the properties of acids in perfection. The class of acids being perfectly arbitrary, there cannot be such a thing as an acidifying principle in the most extensive sense of the word.

Berthollet has lately proposed a definition of acid, which, though not unexceptionable, gives us, I think, more precise notions of this class of bodies than those formerly entertained. Acids, according to him, are bodies capable of combining with alkalies, and of neutralizing them, while, at the same time, they lose their acidity \*. According to this notion, the capacity of neutralizing each other constitutes the essential characters both of acids and alkalies; and that acid which is capable of neutralizing the greatest quantity of alkali possesses the character of acidity in greatest perfection. Were this definition admitted, several bodies at present arranged among acids would be excluded from that class. The greatest objection to it is the existence of some substances which occasionally act the part both of acids and

\* Statique Chemique, i. 69.

Bairrich

#### PRIMARY COMPOUNDS.

Book II. Division II. alkalies, and ought therefore to belong to both sets of substances. But perhaps these bodies (the metallic oxides) do not rigidly neutralize alkalies, and therefore approach more closely to that class. Besides, we can scarcely expect perfect precision in our arbitrary classifications.

Division of acids.

As he class of acids comprehends under it a considerable number of bodies, the subdivision of them under subordinate heads will be attended with considerable advantage. Now, all the acids, like the oxides, are either products of combustion, or supporters of combustion, or combustible. And upon examination, it must appear evident that each of these classes possesses such characters of distinction as to warrant their being con-I shall therefore divide the acids sidered separately. into the three following classes : 1. Products ; 2. Supporters; 3. Combustibles. The acids belonging to the two first classes have only a single base; but those belonging to the third have usually two or more bases, and are sometimes destitute of oxygen. do a local theirs, while, at the same time, they lote their minut

According to this, potion, the capacity or source ling each other constitutes they essential characters both of acids and alkalies; and that and which is capable of neutralizing the groatest quantity of alkali-possesses the character of acidity in groutest part course. While this definition admitted, several bodies of a room arranged among weids would be evaluated from that class. The greatest objection to his the existence of some substanand grantest bodies in a fact and that

#### ACIDS.

nation out r that which contains the maximum, by the termination of ... Thus the seld of sulphur, with a pri-

phur, with a maximum of extrem, is relation and

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# OF ACID PRODUCTS.

The acid products at present known are only five in

number : but I an obliced to add to them from anala-

gy, two other acids, which have not hitlerto been de-

ALL the acids which belong to this class possess the following properties.

1. They may be formed by combustion. Of course their base is a combustible substance.

Properties:

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diois.

2. They are incombustible.

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The two last

3. They cannot be decomposed by the action of the most violent heat which can be applied \*.

4. They are all decomposible by the joint action of a combustible body and caloric.

5. Oxygen is an essential ingredient in all of them. To them, therefore, the theory of Lavoisier applies with precision.

Some of the simple combustibles are capable of combining with two doses of oxygen, and forming acids with each. When that happens, the acid containing the minimum of oxygen is distinguished by the termi-

Prom this Table to is obvient that the active helometing

\* To this property there are some exceptions. It appears from the late experiments of Gay-Lussac that sulphuric acid is decomposable by heat. Mem. d'Arcueil, i. 215.

the fully show the state of

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Chap. II.

Book 11. Division 11. nation ous; that which contains the maximum, by the termination *ic*. Thus the acid of sulphur, with a minimum of oxygen, is *sulphurous* acid; the acid of sulphur, with a maximum of oxygen, is *sulphuric* acid. But it must be remarked, that this mode of distinguishing the doses of oxygen in acids is restricted to the first class of acids, and does not apply to the other two classes, except in one instance.

Names and composition.

Propertion.

The acid products at present known are only five in number: but I am obliged to add to them, from analogy, two other acids, which have not hitherto been decompounded, but whose properties bear a much closer resemblance to the products than to any of the other classes of acids. The following TABLE exhibits the names and constituent parts of these acids as far as they have been ascertained.

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t the	by tasman ion o	boso Bases.	Proportion of oxygen to 100 base.
30 no	Sulphuric di Sulphurous	Sulphur	136*5 88*6
hem. with	Phosphoric <sup>on</sup> Phosphorous	Phosphorus	114.7
- atop	Carbonic	Carbon	257
acids itting	Fluoric braz Boracic	Unknown	ng with two d

From this Table it is obvious that the acids belonging to this class are named from their bases. The two last, the component parts of which are unknown, are denominated from the substances which contain them most abundantly.

SECT. I.

#### OF SULPHURIC ACID.

THOUGH the ancients were acquainted with some of the compounds into which sulphuric acid enters, alum; for instance, and green vitriol, they appear to have been ignorant of the acid itself. It is first mentioned in the works of Basil Valentine, which were published about the end of the 15th century. 'It was for a long time obtained by distilling green vitriol, a salt composed of sulphuric acid and black oxide of iron; hence it was called oil of vitriol, and afterwards vitriolic acid. Another method of obtaining it was by burning sulphur under a glass bell; hence it was called also oleum sulphuris per campanam. The French chemists, in 1787. when they formed the new chemical nomenclature, gave it the name of sulphuric acid.

1. At present it is generally procured by burning a Preparate mixture of sulphur and nitre in chambers lined with lead. The theory of this process is still somewhat obscure. When sulphur is burnt in the open air or in oxygen gas, however high the temperature, only sulphurous acid is produced, and no appreciable quantity of sulphuric acid. If the sulphur be mixed with black oxide of manganese or any metallic oxide which readily parts with its oxygen, the combustion is more brilliant, but still sulphurous acid only is produced. No other Vol. II. M

tion.

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Book II. Division II.

method is known of producing sulphuric acid by the combustion of sulphur, excepting mixing it with nitrate Now the difficulty is to explain the part of potash. which the nitre acts. The quantity used varies from a fifth to a tenth of the sulphur burnt; and according to the experiments of Chaptal, the best proportion is a seventh \*. Now the whole oxygen contained in this portion of nitre does not exceed the seventh part of the oxygen necessary to convert the sulphur into sulphuric acid. It is obvious, therefore, that the necessity of the nitre does not arise from its supplying the requisite quantity of oxygen. The most probable explanation has been furnished by Clement and Desormes. According to them, the nitric acid in the nitre is decomposed by the combustion, deprived of a portion of its oxygen, and emitted in the state of nitrous gas, while the sulphur is converted into sulphurous acid gas, which flies off mixed with the nitrous gas. The nitrous gas absorbs oxygen from the air of the apartment, and is converted into nitric acid, which immediately gives out its oxygen to the sulphurous acid and converts it into sulphuric acid. The nitrous gas is thus formed a second time; it absorbs oxygen a second time, and gives it away as before; and this process is repeated till the whole sulphurous acid is converted into sulphuric acid t.

The sulphuric acid, when first formed, is very weak, being diluted with the water necessary for condensing it; but it is made stronger by distilling off a portion of this water. By this process it is made quite trans-

\*\* Chimie appliquée aux arts. ili. 40. + Ann. de Chim. lix. 329.

#### SULPHURIC.

parent; but it still contains a little lead, which it dissolved from the vessels in which it was manufactured, and a little potash, which it acquired from the nitre employed in burning the sulphur. To obtain it in a state of complete purity, the sulphuric acid of commerce must be distilled. This is easily done by putting it into a small retort with a long beak. The bottom of the retort is placed upon a fire of charcoal, and fixed steady by means of an iron ring; while its beak is plunged half way into a receiver, whose mouth it fits nearly, but not exactly. The acid soon boils, and is gradually condensed in the receiver. Too great a quantity should not be distilled at once, otherwise the retort generally breaks in consequence of the violent agitation into which the boiling acid is thrown.

2. Sulphuric acid is a liquid somewhat of an oily con- Properties. sistence, transparent and colourless as water, without any smell, and of a very strong acid taste. When applied to animal or vegetable substances, it very soon destroys their texture.

It always contains a quantity of water; part of which, however, may be driven off by the application of a moderate heat. This is called concentrating the acid. When as much concentrated as possible, its specific gravity is said to be 2.000; but it can seldom be obtained denser than 1.85.

It changes all vegetable blues to a red except indigo. According to Erxleben, it boils at 546°; according to Bergman, at 540°\*.

When exposed to a sufficient degree of cold, it crys-

# Bergman, il. 152.

Chap. JI.

Book II. Division II.

tallizes or freezes; and after this has once taken place. it freezes again by the application of a much inferior cold \*. Morveau froze it at -4°; it assumed the appearance of frozen snow. After the process began, it went on in a cold not nearly so intense. The acid melted slowly at 27.5°; but it froze again at the same temperature, and took five days to melt in the temperature of 43° 1. Chaptal, who manufactured this acid, once observed a large glass vessel full of it crystallized at the temperature of 48°. These crystals were in groups, and consisted of flat hexahedral prisms, terminated by They felt hotter than the sura six-sided pyramid. rounding bodies, and melted on being handled §. Chaptal has observed, that sulphuric acid, in order to crystallize, must not be too concentrated. This observation has been extended a good deal further by Mr Keir. He found that sulphuric acid, of the specific gravity of 1.780, froze at 45°; but if it was either much more or much less concentrated, it required a much greater cold for congelation ||. When as concentrated as possible, I find that it may be cooled down in thermometer tubes to the temperature of  $-36^{\circ}$  before it congeals ¶.

Action of water. 3. Sulphuric acid has a very strong attraction for water. Neuman found, that when exposed to the atmosphere it attracted 6.25 times its own weight. Mr Gould found, that 180 grains of acid, when exposed to the atmosphere, attracted 68 grains of water the first day, 58 the second, 39 the third, 23 the fourth, 18 the

\* The freezing point was ascertained by the Duc d'Ayen in 1776. See Macquer' Dictionary.

- ‡ Encycl. Method. Chim. i. 376.
- ||. Pbil. Trans. lxxvii. Part'ii.

§ Jour. de Phys. XXII. 473: ¶ See Vol. I. p. 523.

TSO

#### SULPHURIC.

fifth, and at last only 5, 4, 3, 4, 3, &c. The 28th day the augmentation was only half a grain \*. The affinity therefore between sulphuric acid and water, as is the case in general with other substances, becomes weaker the nearer it approaches to saturation. He does not specify the specific gravity of his acid; but as it only attracted 3.166 times its own weight, it could not have been very concentrated.

The affinity between sulphuric acid and water becomes still more striking when these bodies are mixed together. If four parts of sulphuric acid and one part of ice, both at the temperature of 32°, be mixed together, the ice melts instantly, and the temperature of the mixture becomes 212°. On the other hand, if four parts of ice and one part of acid, at 32°, be mixed together, the temperature sinks to about -4°. The cause of this change of temperature has been already explained. When four parts of acid and one part of water are mixed together, the temperature of the mixture rises to about 300° +. The density of this compound of acid and water is much greater than the mean. Heat is also evolved when other proportions of acid and water are mixed together, though not in so great quantity. Lavoisier and De la Place found, that when 2.625lbs. troy of sulphuric acid, of the specific gravity 1.87058, were mixed with 1.969lb. troy of water, as much caloric was evolved as melted 4.1226 lbs. troy of ice, or as much caloric as the acid and water would have given out had they been heated without mixture to 155.9° 1.

We have no reason to suppose that sulphuric acid, at

\* Pbil. Trans. 1684. ‡ Mam. Par. 1780. + Fourcroy, ii. 65.

Chap. II.

Book II. Division II. Strength at various

densities.

the density of 2.000, is free from all mixture of water; so far from that, we know for certain that it contains a considerable proportion; for when it is combined with other bodies (barytes, for instance, or potash), there is a considerable quantity of water which remains behind, and does not enter into the combination. Now, is it possible to determine how much real acid and how much water are contained in a given quantity of acid of a given specific gravity? Attempts were made to answer this important question by Homberg, by Bergman, by Wenzel, and by Wiegleb; but the differences between their determinations were too great to place any confidence in their accuracy. The subject has lately been resumed, and prosecuted with much industry and skill by Mr Kirwan, whose results may be considered as approaching as nearly to perfect accuracy as the present state of the science admits. His method was as follows : He dissolved 86 grains of potash in water, and saturated it exactly with sulphuric acid of a given specific gravity (we shall suppose of 2.00), and diluted it with water till its specific gravity was 1.013. The whole weight amounted to 3694 grains. Forty-five grains of sulphate of potash, dissolved in 1017 grains of distilled water, have the same specific gravity at the same temperature; whence it follows, that the proportion of salt in each was equal. But in the last solution the quantity of salt was  $\frac{1}{22\cdot 6}$  of the whole; therefore the quantity of salt in the first was  $\frac{3694}{22.6} = 159.52$ grains. Now of this weight 86 grains were alkali; the remainder, therefore, which amounts to 73.52 grains,

must be acid. But the quantity of acid employed was

#### SULPHURIG.

"79. grains; of this there were 6.52 grains which did not Chap II. enter into the combination, and which must have been pure water : 79 parts of acid, of the specific gravity 2, therefore, contain at least 6.52 parts of water; and consequently 100 parts of it contain 8.25 parts of water. It only remains now to consider how much water sulphate of potash contains. Mr Kirwan thinks it contains none, because it loses no weight in any degree of heat below ignition; and even when exposed to a red heat for half an hour it hardly loses a grain. This is certainly sufficient to prove, at least, that it contains very little water; and consequently we may conclude, with Mr Kirwan, that 100 parts of sulphuric acid, of the specific gravity 2.000, are composed pretty nearly of 91.75 of pure acid and 8:25 of water.

Since there is such a strong affinity between sulphuric acid and water, and since the density of the mixture is different from the mean density of the ingredients, it becomes a problem of the greatest importance to determine how much of the strongest sulphuric acid that can be prepared exists in any given quantity of sulphuric acid of inferior specific gravity, and which consequently consists of a determinate quantity of this strong acid diluted with water.

This problem has been solved by Mr Kirwan\*. He took sulphuric acid of the specific gravity 2.000, which is the strongest that can be procured, for his standard, and the point was to determine how much of this stand-

\* Irisb Trans. iv. 18.

Book II. Division II.

ard acid existed in a given quantity of acid of inferior density.

He concluded, from a number of experiments with sulphuric acid, of the specific gravities 1.8846, 1.8689, 1.8042, 1.7500 (for he could not procure an acid of the specific gravity 2.000 at the temperature of 60°, in which his experiments were performed), that when equal parts of standard acid and water are mixed, the density is increased by  $\frac{1}{75}$ th part of the whole mixture, Then, by applying a formula given by Mr Poujet\*<sub>a</sub> he calculated, that the increase of density, on mixing

onelude. N

\* Mr Poujet undertook the examination of the specific gravity of alcohol mixed with different quantities of water. He took for his standard alcohol whose specific gravity was 0.8199, at the temperature of 65.75°. He then formed ten mixtures; the first containing nine measures of alcohol and one of water, the second eight measures of alcohol and two of water, and so on till the last contained only one measure of alcohol and nine of water. He took care that each of these measures should contain equal bulks, which he ascertained by weight, ebserving that a measure of water was to a measure of alcohol as 1 to 0.8190. Thus 10000 grains of water and 8199 of alcohol formed a mixture containing equal bulks of each. From the specific gravity of each of these mixtures he discovered how much they had diminished in bulk in consequence of mixture, by the following method:

Calling A the real specific gravity of any of the mixtures; B its specific gravity found by calculation, supposing no diminution of bulk; n the number of measures composing the whole mass; n - x the number to which it is reduced in consequence of mutual penetration—it is evident, since the increase of density does not diminish the weight of the whole mass, that  $n = \overline{n - x} \times A$ . Therefore  $x = \frac{A - B}{A} \times n$ , or (making n = 1) =  $\frac{A - B}{A}$ .  $\frac{A - B}{A}$  is therefore the diminution of volume produced by the mixture.

The following TABLE contains the result of Mr Poujet's experiments, calculated according to that formula; the whole volume or n being = 1

#### SULPHURIC.

different quantities of standard acid and water, was as Chap. II. in the following TABLE:

Measures of Water. Alcohol.		Diminution of the whole vo- lume = 1 by experiment.	By calculation.
I	9	0.0100	0.0103
2	8	0.0182	0.0184
3		00242	0.0242
4	6	0.0268	0.0276
5	5	0.0288	a market a start
6	i De 4 Sw	0.0266	0.0276
7	3	0.0207	0.0242
8	2	0.0123	0.0184
9	The Lat	0.0044	0.0103

while the pressures of alcohol are more than these of

It is evident, from this Table, that the diminution of the bulk of the mixture follows a regular progression. It is greatest when the measures of water and alcohol are equal, and diminishes as it approaches both ends of the series. Mr Poujet accounts for this by conceiving the alcohol to be dissolved in the water, which retains a part of it in its pores, or absorbs it. The quantity absorbed ought to be in the ratio of that of the solvent and of the body dissolved, and each measure of water will retain a quantity of alcohol proportional to the number of measures of alcohol in the mixture. Thus in a mixture formed of nine measures of alcohol and one of water, the water will contain a quantity of alcohol = 9; in one of eight measures of alcohol and two of water, the water will contain a quantity of alcohol = 8. Therefore the diminution of bulk in each mixture is in a ratio compounded of the measures of alcohol and water which form it, in the Table given above, as I X 9, 2 X 8, 3 X 7, 4 X 6, &c. And in general, taking the diminution of bulk when the measures of both liquids are equal for a constant quantity, and calling it c, calling the number of measures n, the number of measures of alcohol x, the in-

water.	parts of stan- dard acid.	Augmenta- tion of den- sity.
5	95	0.0252
10	90	0.0479
15	85	0.0679
20	80	0.0856
25	75	0.0999
30	70	0.1119
35	65	0.1213
40	60	0.1279
45	55	0.1319
50	50	0.1333
	5 10 15 20 25 30 35 40 45	5         95           10         90           15         85           20         80           25         75           30         70           35         65           40         60           45         55

Book II. Division II.

crease of density or diminution of bulk z; we shall have  $e: z::\frac{n}{2} \times \frac{n}{2}$ 

 $: \overline{n-x} \times x \text{ and } z = \frac{4c}{n^2} \times \overline{n \ x-x^2}, \text{ or (making } n=1) = 4 \ c \ x-4 \ c \ x^2.$ 

The diminution of bulk, calculated according to this formula, makes the last column of the Table in this note. They correspond very well with experiment, while the measures of alcohol are more than these of water, but not when the reverse is the case. This Mr Poujet thinks is owing to the attraction which exists between the particles of water, and which, when the water is considerable compared with the alcohol, resists the union of the water with the alcohol.

By the formula  $z = \frac{4 c n x - 4 c x^2}{n^2}$ , the quantity of alcohol of the standard may be determined in any mixture where the alcohol exceeds the water.

Let the number of measures, or the whole mass - = r
The measures of alcohol
The diminution of bulk at equal measures $  = c$
The diminution of bulk of a mixture containing #
measures of alcohol = $4 c x^2$
The specific gravity of water - = a
The specific gravity of the alcohol $ = b$
The specific gravity of the unknown mixture y
Then since the increase of density does not change the weight of the

#### SULPHURIC.

By adding these augmentations to the specific gravity Chap. II. of the above mixture, found by calculation, and taking the mean for the intermediate quantities, he drew up a table of the quantity of acid of the density 2.00, contained in a given weight of acid of inferior density, from 2 to 1.4666. Sulphuric acid of this last density contains just 0.5 of sulphuric acid of 2. The quantity contained in acids of inferior densities was ascertained from actual observation. He found by the first part of the table, that 100 parts of acid, of the specific gravity 1.8472, contained 88.5 parts standard; consequently 400 grains of this acid contain 354 grains standard. He took six portions of this acid, each containing 400 grains, and added to them as much water as made them contain respectively 48, 46, 44, 42, 40, 38 grains standard. The quantity of water to be added, in order to produce this effect, he found by the following method: Suppose x = the quantity of water to be added to 400 parts of acid, that the mixture may contain 48 per cent. of standard acid. Then 400 + x : 354 : : 100 : 48, and consequently x = 337.5. After finding the specific gravity of these, the half of each was taken out, and as

whole, 
$$\overline{1 - x} \times a + b \times = \overline{1 - 4c \times 4 4 c x^2} \times y$$
.  
Hence  $x = 0.5 - \frac{a - b}{8cy} + \sqrt{\frac{a - y}{4cy} + (\frac{a + b}{8cy} - 0.5)}$   
 $y = \frac{a - a \times + b \times}{1 - 4c \times 4 c \times^2}$   
And making  $a = 1, b = 0.8199, c = 0.0288$   
 $x = 0.5 - \frac{0.1801}{0.2304y} + \sqrt{\frac{1 - y}{0.1152y} + (\frac{0.1801}{0.2304y} - 0.5)}$   
 $y = \frac{1 - 0.1801 \times}{1 - 0.1152 \times + 0.1152 \times^2}$ . See Irish Trans.

Book II-Division II. much water added; and thus the specific gravities corresponding to 24, 23, 22, 21, 20, 19, were found. Then six more portions, of 400 grains each, were taken, of the specific gravity 1.8393, and the proper quantity of water added to make them contain 36, 34, 32, 30, 28, 26 per cent. of standard. Their specific gravities were found, the half of them taken out, and as much water added; and thus the specific gravity of 18, 17, 16, 15, 14, and 13 found. Care was taken, after every addition of water, to allow the ingredients sufficient time to unite.

By multiplying the standard acid, as ascertained in this Table, by 0.8926, he obtained the quantity of real acid contained in sulphuric acid of different densities at the temperature of 60°. This may be seen in the following TABLE\*.

the second second second second		and the second se	and the second second
100 Parts	Real	100 Parts	Real
Sp. Gravity.	Acid.	Sp. Gravity.	Acid.
			- dia generalia
2.0000	89.29	1:8070	75.89
1'9859	88.39	1.7959	75
1.9719	87.50	1.7849	74.11
1.9579	86.61	1.7738	73.22
1.9439	85.71	1.7629	72.32
1.9299	84.82	1·7519	71.43
1.9168	83.93	1.7416	70.54+
1.9041	83.04+	1.7312	69.64
1.8914	82.14	1.7208	68:75
1:8787	81.25	1.7104	67.86
1.8660	80.36	1.7000	66.96
1.8542	79.46	1.6899	66.07
1.8424	78.57	1.0800	65.18
1.8306	77.68	1.6701	64.28
1.8188	76.79+	1.6602	63.39

Strength of sulphuric acid.

\* Nicholson's Journal, iii. 213.

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T	100 Parts	Real	100 Parts	Real
S	p. Gravity.	Acid.	Sp. Gravity.	Acid.
-				
	1.6503	62.50	1.2921	31.25
F	1.6407	61.61	1.2847	30.35
	1.6312	60.71	1.2757	29.46
	1.6217	59.82	1.2668	28.57+
1	1.6122	58.93	1.2589	27.68
	1.6027	58.03	1.2510	26.78
Ł	1.5932	57.14	1.2415	25.89
	1.5840	56.25	1.2320	25 -
1	1.5748	55.36+	1.2210	24.10
1	1.5656	54.46	1.2101	23.21
1	1.5564	53.57	1.2009	22.32
1	1.5473	52.68	1.1918	21.43
1	1.5385	51.78	1.1836	20.53+
	1.5292	50.89	1.1746	19.64
	1.5202	50.00	1.1678	18.75
	1.5112	49.11+	1.1614	17.85
1	1.5022	48.21	1.1531	16.96
	1.4933	47.32	1.1398	16.07
1	1.4844	46.43	1.1309	15.18+
1	1.4755	45.53	1.1208	14.28
1	1.4666	44.64	1.1129	13.39
1	1.4427	43.75	1.1011	12.50
	1.4189	42.86+	1.0955	11.60
	1.4099	41.96		
	1.4010	41.07	1.0896	10.71
	1.3875	40.18	1.0833	9.80
-	1.3768	39.28	1.0780	8.93+
ł	1.3663	38.39	1.0725	8.03
	1.3586	37.50	1.0666	7.14
1	1.3473	36.00	1.0610	6.25
	1.3360	35.71	1.0555	5.35
	1.3254	34.82	1.0492	4.46
1	1.3149	33.93	1.0450	3.57
1	1.3102	33.03	1.0396	2.67
1	1.3056	32.14	1.0343	1.78
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Book II. Division II. Its compo-

4. Mr Lavoisier attempted to ascertain the proportion of the constituents of this acid, by measuring the quantity of oxygen absorbed by a given weight of sulphur during its combustion. His result was 71 parts of sulphur and 29 of oxygen. But this method was not susceptible of sufficient precision to warrant much confidence. Mr Thenard had recourse to a much better method \*, which was employed still more lately for the same purpose by Mr Chenevix with much address +. Nitric acid was distilled off 100 parts of pure sulphur repeatedly till the whole sulphur was converted into an acid. The sulphuric acid, thus formed, was separated by means of barytes, with which it forms an insoluble compound. The 100 parts of sulphur, thus acidified, vielded 694 parts of dry sulphate of barytes. Hence 100 parts of sulphate of barytes contain 14.5 parts of sulphur. This experiment was repeated by Klaproth with the same result. To know the portion of oxygen in sulphuric acid, it is only necessary to know the weight of sulphuric acid contained in dry sulphate of barytes. A great many experiments have been made to determine that point. Here Mr Chenevix seems to have fallen into an error. He makes it only 24 per. cent. The analysis of Thenard indeed nearly agrees with his; but all other chemists make it above 30 per cent. I consider the result obtained by Kirwan and Klaproth as the most accurate. They coincide, and find sulphate of barytes composed of 33 parts sulphuric acid and 67 of barytes. Hence it follows, that sulphuric acid

\* Ann. de Chim. xxxii. 266. † Irish Trans. 1802, p. 233:

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sition.

#### SULPHURIC.

is composed of 14.5 of sulphur, and 18.5 of oxygen; Chap. II. or of

42.3	sulphur
57.7	oxygen
	backdin

100.0

or 100 sulphur and 136.5 oxygen\*.

5 Sulphuric acid is not altered by the action of light Action of nor caloric. It does not combine with oxygen. It was oxygen, affirmed indeed by some chemists, that sulphuric acid might be combined with oxygen by distilling it off the black oxide of 'manganese; but the assertion was refuted by the experiments of Vauquelin.

6. None of the simple combustibles act upon it at the Of the sime usual temperature of the atmosphere, or at least their tibles. action is so slow as not to be perceptible : But when they are assisted by heat, they are all capable of deposing it.

When sulphur is boiled in this acid, it absorbs a portion of its oxygen, or at least combines with it, and the whole is converted into sulphurous acid. Phosphorus also absorbs oxygen from it by the assistance of heat, sulphurous acid is driven off, and phosphoric acid formed. At the boiling temperature charcoal also absorbs oxygen from it, and converts it into sulphurous acid. At a red heat it even converts it into sulphur. When hydrogen gas and sulphuric acid are made to pass together through a red hot tube of porcelain, the acid is completely decomposed, water is formed, and sulphur deposited +.

\* Gehlen's Jour. v. 509 ..

+ Fourcroy, ii. 62.

ple combus-

Book II. Division II. Of the incombustibles, 7. Azote has no action on sulphuric acid; but this acid readily absorbs muriatic acid, and forms with it a liquid of a brownish tinge, which emits the dense and suffocating odour of muriatic acid, and corrodes vegetable and even metallic bodies near which it happens to be placed.

Of metals,

8. When zinc or iron is thrown into sulphuric acid. a violent action takes place, if the acid be diluted ; water is decomposed, its hydrogen flies off, and its oxygen combines with the metals. If the acid be concentrated, the action is much less violent, and sulphurous acid exhales. Upon tin and copper the acid acts very slowly and feebly, unless its action be assisted by heat when it oxidizes and dissolves them. On silver, mercury, antimony, bismuth, arsenic, and tellurium, it does not act except at a pretty high temperature. These metals abstract part of its oxygen, and convert one portion of it to sulphurous acid, while another portion combines with the oxides thus formed. When boiling hot it oxidizes lead, and dissolves cobalt, nickel, and molybdenum: But it has no perceptible action on gold nor platinum at any temperature to which it can be raised.

Of alkalies and earths. 10. It unites readily with all the alkalies and earths except silica, and with most of the metallic oxides, and forms salts denominated *sulphates*. Thus the combination of sulphuric acid and soda is called *sulphate of soda*; the compound of sulphuric acid and lime, *sulphate of lime*, and so on.

11. It absorbs a very considerable quantity of nitrous gas, and acquires by that means a purplish colour \*.

\* Priestley, i. 389.

#### SULPHUROUS.

This is one of the most important of all the acids, not only to the chemist but to the manufacturer also; being employed to a very great extent in a variety of manufactures, especially in dyeing.

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# OF SULPHUROUS ACID.

THOUGH some of the properties of this acid must have History. been known in the remotest ages, as it is always formed during the slow combustion of sulphur, Stahl was the first chemist who examined it, and pointed out its peculiar nature. He gave it the name of phlogisticated sulphuric acid, from the supposition that it is a compound of sulphuric acid and phlogiston. His method of procuring it was to burn sulphur, and expose to its flames cloth dipped in a solution of potash. By this method he obtained a combination of potash and sulphurous acid; for sulphur forms by combustion only sulphurous acid. Scheele pointed out, in 1771, a method of procuring sulphurous acid in quantities \*. On Stahl's salt he poured a portion of tartaric acid, and then applied a gentle heat. The sulphurous acid is in this manner displaced, because its affinity for potash is not so strong as that of tartaric acid; and it comes over in-

\* Scheele, i. 43.

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Chap. II.

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Book II. Division II. to the receiver dissolved in water. Dr Priestley, in 1774, obtained it in the gaseous form, and examined its properties while in a state of purity\*. Berthollet pubished a dissertation on its formation, composition, and uses, in 1782 and 1789 †; and in 1797 appeared a very complete dissertation on its combinations by Fourcroy and Vauquelin ‡.

Preparasion. 1. Sulphurous acid may be procured by the following process: Put into a glass retort two parts of sulphuric acid and one part of mercury, and apply the heat of a lamp: The mixture effervesces, and a gas issues from the beak of the retort, and may be received in glass jars filled with mercury, and standing in a mercurial trough. This gas is sulphurous acid.

Properties.

2. Sulphurous acid, in the state of gas, is colourless and invisible like common air. It is incapable of maintaining combustion; nor can animals breathe it without death. It has a strong and sulfocating odour, precisely the same with that exhaled by sulphur burning with a blue flame: sulphur, by such a combustion, being totally converted into sulphurous acid. Its specific gravity, according to the experiments of Kirwan, is 2.265, that of air being 1.000: At the temperature of .60°, barometer 30 inches, 100 cubic inches of this gas weigh 70.215 grains ||.

3. This acid reddens vegetable blues, and gradually destroys the greater number of them. It exercises this power on a great variety of vegetable and animal colours. Hence the use of the fumes of sulphur in bleach-

\* On Air, ii. 295. + Mem. Par. 1782. Ann. de Chim. ii. 54. 1. Ann. de Chim. XXIV. 229. || Kirwan on Phlogiston, p. 30.

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#### SULPHUROUS.

ing wool and in whitening linen stained by means of Chap. II. fruits.

Planche has observed, that when syrup of violets, previously reddened by acids, is mixed with a little sulphurous acid, the original blue colour of the syrup is restored, and its intensity gradually diminishes \*.

4. Dr Priestley discovered, that when a strong heat is applied to this acid in close vessels, a quantity of sulphur is precipitated, and the acid is converted into sulphuric +. Berthollet obtained the same result; but Fourcroy and Vauquelin could not succeed 1.

According to Clouet and Monge, when this gas, in a state of condensation, is exposed to the temperature of -18°, it is condensed into a liquid §.

5. Water absorbs this acid with rapidity. According Action of to Dr Priestley, 1000 grains of water, at the temperature 54.5°, absorb 39.6 grains of this acid. Fourcroy, on the other hand, affirms, that water at 40° absorbs the third of its weight of sulphurous acid gas ¶. Upon trying the experiment, I found that one cubic inch of water at the temperature of 61°, barometer 29.55 inches, absorbs 33 inches of gas. But an inch of water weighs about 253.175 grains, and 33 inches of this gas weigh 23.16. Hence it follows, that 1000 water in weight absorbs 91.5 of this gas. This exceeds considerably the estimate of Priestley, though it comes short of that of Fourcroy. Water impregnated with this gas acquires, according to my experiments, the specific gravity 1.0513, even in as high a temperature as 68°. This

water.

\* Ann. de Chim. 1x. 253. + On Air, ii. 330. § Fourcroy, ii. 74.

+ Nicholson's Journal, i. 313. ¶ Ibid. p. 77. Nº

Book H. Division II. water may be frozen without parting with any of the acid gas. When water, which has been saturated with this acid at the freezing temperature, is exposed to the heat of  $65 \cdot 25^{\circ}$ , it is filled with a vast number of bubbles, which continually increase and rise to the surface. These bubbles are a part of the acid separating from it. It freezes a few degrees below  $32^{\circ}$ \*.

Of oxygen and air, 6. When liquid sulphurous acid is exposed to atmospheric air or to oxygen gas, it gradually combines with oxygen, and is converted into sulphuric acid. This change takes place more completely if the acid be combined with an alkali or earth. When a mixture of sulphurous acid gas and oxygen gas is made to pass through a red hot porcelain tube, the two bodies combine, and sulphuric acid is formed  $\ddagger$ .

Of the other simple bodies, 7. Of the simple combustibles, sulphur and phosphorus have no action on it whatever; hydrogen gas and charcoal do not alter it while cold, but at a red heat they decompose it completely: water or carbonic acid is formed, and sulphur deposited  $\ddagger$ .

8. Neither azote nor muriatic acid produce any change on it.

9. Sulphurous acid does not seem capable of oxidizing or dissolving any of the metals except iron, zinc, and manganese,

10. It combines with alkalies, earths, and metallic oxides, and forms salts known by the name of sulphites.

11. Sulphyric acid absorbs this gas in considerable

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Of sulphusic acid.

\* Fourcroy and Vauquelin, Nicholson's Jour. i. 313.

- † Priestley, ii. 332. Fourcroy, ii. 74.
- ‡ Fourcroy and Vauquelin.

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quantity. It acquires a yellowish brown colour, a penetrating odour, and the property of smoking when exposed to the air. When this mixture is distilled, the first vapour which comes over, and which is a compound of the two acids, crystallizes in long white prisms. This singular compound, formerly known by the name of glacial sulphuric acid, smokes in the air; and when the atmosphere is moist, melts with effervescence. When thrown into water, it hisses like a red hot iron. It has the odour of sulphurous acid \*. This curious compound, first mentioned by Kunkel, and afterwards by Bohn and by Neuman, attracted a great deal of the attention of chemists, who attempted to investigate the cause of its singular properties. The general opinion, in consequence of the experiments of Hellot, Wiegel, Meyer, and Gottling, was, that phlogiston, some how or other, contributed to its produc-Dolfusz + made a set of experiments on it in tion. 1784; from which he concluded that it was peculiar to sulphate of iron, by the distillation of which it had been usually procured. These experiments were repeated and varied by Morveau 1; and this philosopher considered it as probable that the glacial acid is merely sulphuric acid, totally deprived of moisture. Fourcroy has lately demonstrated that it is a compound of sulphuric and sulphurous acids."

12. As this acid is formed by the combustion of sulphur, it cannot be doubted that it is composed of the same ingredients with sulphuric acid; and as it is evol-

Composition.

Chap. II.

<sup>\*</sup> Fourcroy, ii. 78. † Crell's Annals, 1785, i. 438. # Encyc. Method. Chim. i. 390.

Book II. Division II. ved from sulphuric acid by the action of sulphur, and likewise by some of the metals, it cannot be doubted that it contains a smaller proportion of oxygen. I endeavoured to estimate the constituents of this acid in the following manner: By causing a current of sulphurous acid gas to pass through a solution of carbonate of potash in water, I formed the salt called sulphite of potash. When this salt, previously dried upon bloating paper, is exposed to the heat of 300°, it loses 3:3 per cent. of its weight. When 100 grains of it are heated to redness in a platinum crucible, the salt decrepitates, becomes of an opaque white, and emits a blue flame. By this treatment it loses 22.3 per cent. and leaves as a residuum sulphate of potash. This sulphate of potash contains 22.25 of sulphuric acid, the rest is potash. From this analysis it follows that sulphite of potash is composed of the second states a work or so that

22°30 volatile matter de Constant 22°25 sulphuric acidemont de Constant 55°45 potash anon lo standare e

been usually proceed.

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When 100 grains of sulphite of potash are heated in a retort attached to a mercurial apparatus, there come over 18 cubic inches of sulphurous acid gas, 5:1 grains of sulphur, and a little water. The remaining salt weighs 77.7 grains, and contains 23:2 sulphuric acid, the rest potash. From this analysis it follows that the 100 grains of sulphite of potash were resolved into

## SULPHURODS.

23.2 sulphuric acid

5.1 sulphur

54.5 potash

17.2 sulphurous acid and water

But the 23.2 sulphuric acid and 5.1 of sulphur must have been united in the salt, and formed sulphurous acid. Of course, sulphurous acid is composed of 23.2 sulphuric acid and 5.1 sulphur, or, per cent. of

82 sulphuric acid

18 sulphur

But as we know the constituents of sulphuric acid, it is easy thence to deduce the following as the proportion. of the ingredients of sulphurous acid :

53 sulphur 47 oxygen

contrast the the water ; but 100 and may be ever

or 100 sulphur and 88.6 oxygen.

# SECT. III.

OF PHOSPHORIC ACID.

**PHOSPHORUS**, like sulphur, forms an acid with two different proportions of oxygen. Combined with a maximum of oxygen, it constitutes *phosphoric* acid;

the statements of signify proof with easy are

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Chap. II.

Book H. with a smaller proportion, it constitutes phosphorous Division II. acid.

> Phosphoric acid remained unknown till after the discovery of phosphorus. Boyle is perhaps the first chemist who mentions it; but Margraff first examined its properties, and demonstrated it to be a peculiar acid. Its properties were afterwards more completely investigated by Bergman, Scheele, Lavoisier, Pearson, Fourcroy, and Vauquelin, and several other distinguished chemists.

Preparation.

1. It may be formed by setting fire to a quantity of phosphorus contained in a vessel filled with oxygen gas. The phosphorus burns with great rapidity, and a great number of white flakes are deposited, which are phosphoric acid in a state of purity. It may be obtained too by heating phosphorus under water till it melt, and then causing a stream of oxygen gas to pass through it by means of a tube. In this case the acid as it forms combines with the water; but the liquid may be evaporated off by the application of heat, and then the acid remains behind in a state of purity. But the usual method of procuring it is to throw phosphorus in small pieces at a time into hot nitric acid. A violent effervescence takes place, the phosphorus combines with oxygen, and nitrous gas is emitted. After the whole of the phosphorus is acidified, the liquid is to be evaporated to dryness, in order to drive off the remains of nitric acid which may not have been decomposed. This process was first put in practice by Lavoisier. Care must be taken not to apply too much heat, not to add too much phosphorus at once, and not to have the nitric acid too strong; otherwise the phosphorus takes fire, and usually breaks the vessels in pieces. When the acid

#### PHOSPHORIC.

prepared by this method is concentrated and heated, it always emits a considerable quantity of phosphureted hydrogen gas, which burns and occasions a considerable loss. This loss may be diminished by cautiously dropping nitric acid into the hot mass.

2. The acid thus prepared may be put into a plati, Properties. num crucible, and heated to redness, to drive off all the water. It is then in a state of purity. It is solid, colourless, and transparent, and not unlike glass in appearance. It reddens vegetable blues; it has no smell; its taste is very acid, but it does not destroy the texture of organic bodies.

When exposed to the open air, it soon attracts moisture, and deliquesces into a thick oily-like liquid; in which state it is usually kept by chemists. When exposed to the fire in a platinum crucible, its water gradually evaporates, and leaves it in the state of a transparent jelly. If the heat be increased it boils and bubbles up, owing to the separation of the remainder of its water, accompanied with a small portion of acid. At a red heat it assumes the form of a transparent liquid, and when cooled resembles the purest crystal. In this state it is known by the name of phosphoric glass. This glass is merely phosphoric acid totally deprived of water. It has an acid taste, is soluble in water, and deliquesces when exposed to the air. At a red heat it evaporates very copiously in a white smoke, which has no strong odour, unless the evaporation be prevented by the presence of a base.

The specific gravity of this acid, in a state of dryness,

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Chap. II.

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Book II. Division II.

Action of water. is 2.687\*; in the state of glass, 2.8516+; in the state of deliquescence, 1.417‡.

3. This acid is very soluble in water. When in the state of white flakes, it dissolves with a hissing noise, similar to that made by red hot iron plunged into water. When in the state of glass it dissolves much more slowly. The heat evolved during the combination of this acid and water is much inferior to that evolved when sulphuric acid enters into a similar combination. Phosphoric acid obtained by deliquescence, when mixed with an equal quantity of distilled water, acquired so little *beat* as to raise the thermometer only one degree, as Mr Sage observed. Mr Lavoisier raised the thermometer from  $50^{\circ}$  to  $63^{\circ}$  by mixing phosphoric acid, boiled to the consistence of a syrup, with an equal quantity of water; and from  $50^{\circ}$  to  $104^{\circ}$  when the acid was as thick as turpentine §.

Action of the combustibles, 4. Oxygen gas has no action on phosphoric acid, whatever be the temperature. Neither is it decomposed or altered by any of the simple combustibles, if we except charcoal  $\P$ ; which, though it has no action on it while cold, at a red heat decomposes it completely; carbonic acid is formed, and phosphorus sublimed. This is the common process for obtaining phosphorus.

5. None of the simple incombustibles have any particular action on it.

Of metals.

6. This acid, when in a liquid state, is capable of oxi-

- \* Bergman's Sciographia, p. 20. Eng. Trans.
- + Hassenfratz, Ann. de Chim. xxviii. 11.
- \$ Encyc. Methor. Chim. i. 221.
- § Keir's Dictionary,

¶ And perhaps also hydrogen; but the experiment has not been made.

## PHOSPHORIC.

dizing some of the metals, especially when assisted by heat; at the same time hydrogen gas is emitted. Hence we see that the oxidizement is owing to the decomposition of water. In this manner it oxidizes iron, tin, lead, zinc, antimony, bismuth, manganese; but on some of these it acts very slowly. When fused with several of these metals, as tin, iron, and zinc, it is converted into phosphorus; a proof that they have a stronger affinity for oxygen.

It does not act upon gold, platinum, silver, copper, mercury, arsenic, cobalt, nickel. It appears, however, to have some action on gold in the dry way, as it is called; for when fused with gold-leaf it assumes a purple colour : a proof that the gold has been oxidized,

7. Phosphoric acid combines with alkalies, earths, phosphates. and metallic oxides, and forms with them salts known by the name of phosphates.

8. The component parts of this acid have been ascer- Compositained in a more satisfactory manner than almost any other chemical compound. Mr Lavoisier deduced from his experiments, that 45 parts of phosphorus, when burnt in oxygen, absorbed about 69°375 parts of that gas, and produced about 114 parts of phosphoric acid \*. But his mode of experimenting was not susceptible of much precision. It consisted in burning phosphorus in oxygen gas, and ascertaining the increase of weight, which he ascribed to oxygen. Mr Rose has lately published an elaborate set of experiments on the constituents of phosphoric acid. He acidified the phosphorus by means of nitric acid, and ascertained the weight by combining

# Lavoisier's Elements, p. 104.

tion.

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the acid formed with oxide of lead. The result of his experiments was, that the acid was composed of

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lead, sinc, antimony, bismath, menuse; but on

some of these it acts very alon 0:001 vie fund with

or 100 phosphorus combines with 114:75 of oxygen, and forms 214.75 of phosphoric acid \*. Some experiments, which I made in the same way nearly, gave me a result a good deal different. I combined the acid formed with lime. But as I do not recollect the proportion of acid which I estimated in phosphate of lime, it is impossible to say how far my results differed from those of Rose.

This acid is too expensive to be brought into common use. If it could be procured at a cheap rate, it might be employed with advantage, not only in several important chemical manufactures, but also in medicine, and perhaps even for the purposes of domestic economy.

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# OF PHOSPHOROUS ACID.

History.

 $T_{HE}$  acid obtained by the burning of phosphorus differs according to the rapidity of the combustion; or, which is the same thing, according to the temperature

\* Gehlen's Jour . 2d Series, ii. 309.

in which the process is conducted. When heated to 148°, it burns rapidly, and the product is phosphoric acid; when allowed to burn gradually, at the common temperature of the air, the product is phosphorous acid. which contains a smaller proportion of oxygen. The difference between these two acids had been remarked by Sage, by Proust, and by Morveau; but it was Lavoisier who first, in 1777, demonstrated that they form different compounds with other bodies, and that the difference between them is owing to the different proportions of oxygen which they contain \*.

1. Phosphorous acid is prepared by exposing phosphorus during some weeks to the ordinary temperature of the atmosphere. Even in winter the phosphorus undergoes a slow combustion, and is gradually changed into a liquid acid. For this purpose, it is usual to put small pieces of phosphorus on the inclined side of a glass funnel, through which the liquor which is formed drops into the bottle placed to receive it. From one ounce of phosphorus about three ounces of acid liquor may be thus prepared. It was called pblogisticated phosphoric acid by Morveau, from the supposition that it is a compound of phosphoric acid and phlogiston.

2. Phosphorous acid, thus prepared, is a viscid liquid, Properties. of different degrees of consistence, adhering like oil to the sides of the glass vessel in which it is contained. It emits the smell of garlic, especially when heated. Its taste is acid like that of phosphoric acid, and it produces the same effect upon vegetable colours. Its specific gravity has not been determined.

Preparation-

\* Mem. Par. 1777.

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Chap. H.

Book II. Division II. 3. It combines with water in every proportion; but it cannot, like phosphoric acid, be obtained in a concrete state.

Action of water. When heated, part of the water which it contains is at first evaporated. Then large bubbles of air rise to the surface; there they break, and emit a dense white smoke, or even take fire if the experiment be performed in an open vessel. The emission of these bubbles of phosphureted hydrogen gas continues for a long time. When the process is finished, the acid which remains is no longer phosphorous, but phosphoric acid. These phenomena show us, that phosphorous acid holds in solution a certain portion of phosphorus, which at a high temperature decomposes water, and is converted partly into phosphoric acid, partly into phosphureted hydrogen.

Of simple bodies.

4. This acid is converted into phosphoric acid by exposure to air or oxygen gas. The process is exceedingly slow, and the conversion is never complete. It succeeds better when the acid is diluted with a great proportion of water \*.

5. Phosphorous acid is not acted upon by any of the simple combustibles except charcoal, and perhaps also hydrogen. Charcoal decomposes it at a red heat as well as phosphoric acid. The products are carbonic acid and phosphorus. It does not act on the simple incombustibles.

6. Its action on metals is exactly similar to that of phosphoric acid, excepting only that the hydrogen gas evolved during the oxidizement of the metals has a fetid smell, and holds phosphorus in solution.

# Fourcroy, ii. 55.

## CARBONIC.

7. It combines with alkalies, earths, and metallic oxides, and forms compounds distinguished by the name Phosphites of phosphites.

8. Sulphuric acid produces no change upon it while Action of cold; but at a boiling heat it parts with some of its oxygen, and the phosphorous acid is converted into phosphoric acid. Nitric acid also, when assisted by heat, converts it readily into phosphoric acid. This furnishes us with by far the best process for obtaining phosphoric acid at present known. Mix phosphorous acid, obtained by slow combustion, with one-eighth of its weight of nitric acid of the specific gravity 1.3, and distil. The nitric acid is decomposed, and pure phosphoric acid remains behind. For this process we are indebted to Fourcroy \*.

This acid has not hitherto been put to any use. The history of its preparation is sufficient to convince us, that it is composed of the same constituents as phosphoric acid : But the exact proportion of these constituents has not hitherto been ascertained.

# SECT. V.

## OF CARBONIC ACID.

As the rapid progress of chemistry, during the latter History. part of the 18th century, was in a great measure owing

\* Fourcroy, J. 86.

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acids

Book II. Division II. to the discovery of this acid, it may be worth while to trace the history of it somewhat particularly.

Paracelsus and Van Helmont were acquainted with the fact, that air is extricated from limestone during certain processes, and the latter gave to air thus produced the name of gas. Hales ascertained the quantity af air that could be extricated from these bodies in different processes, and showed that it formed an essential part of their composition. Dr Black proved that the substances then called lime, magnesia, and alkalies, are compounds, consisting of a peculiar species of air, and pure lime, magnesia, and alkali. To this species of air he gave the name of fixed air, because it existed in these bodies in a fixed state. This air or gas was afterwards investigated by Dr Priestley, and a great number of its properties ascertained. From these properties Mr Keir\* first concluded that it was an acid; and this opinion was soon confirmed by the experiments of Bergman, Fontana, &c. Dr Priestley at first suspected that this acid entered as an element into the composition of atmospherical air; and Bergman, adopting the same opinion, gave it the name of aerial acid. Mr Bewdly called it mephitic acid, because it could not be respired without occasioning death; and this name was also adopied by Morveau. Mr Keir called it calcareous acid ; and at last Mr Lavoisier, after discovering its composition, gave it the name of carbonic acid gas.

For the investigation of the properties of carbonic acid we are chiefly indebted to the labours of Caven-

\* Keir's Macquer, art. Air.

dish \*, Priestley +, Bergman ‡, and Lavoisier §. Va- Chap. II. luable dissertations on it were also published by Macbride ||, Lane ¶, Jacquin \*\*, Landriani ++, Fontana, and many other distinguished chemists.

1. Carbonic acid, being a compound of carbon and Preparaoxygen, may be formed by burning charcoal ; but as it exists in great abundance ready formed, there is no occasion to have recourse to that expedient. All that is necessary is to dilute with water a quantity of chalk, which is a compound of carbonic acid and lime, and to pour upon it sulphuric acid. An effervescence ensues, carbonic acid is evolved in the state of gas, and may be received in the usual manner.

2. Carbonic acid, when in the state of gas, is invi- Properties. sible and elastic like common air. It extinguishes a candle, and is unfit for respiration. It has no smell.

Its specific gravity, according to the experiments of Kirwan, is 1.500, that of air being 1.000; or it is to air as 3 to 2. At the temperature of 60°, barometer 30 inches, 100 cubic inches of this gas weigh 46.5 grains 11. From this considerable weight, compared to that of air, it happens that this gas may be poured from one vessel to another. When poured from a widemouthed vessel upon a burning candle, it extinguishes it like water.

+ Priestley, i: 43. \* Phil. Trans. 1766, lvi. 141. § Mem. Par. 1776. ‡ Opusc. i. I. ¶ Priestley, i. 5. || Experimental Essays, 1764. \*\* Examen. Chem. Dict. Meyer, de Acido Pingui, et Blackiana de Aere Fixo, 1769.

ft Crell's Annals, 1785, ii. 139. Vol. II.

11 Kirwan on Phlogiston, p. 29:

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tion.

Book II. Division II. It reddens the tincture of turnsol, but no other vegetable colour \*.

Atmospheric air is supposed to contain about  $\frac{1}{1600}$  part of this gas  $\dagger$ .

3. Carbonic acid is not altered by exposure to heat in close vessels, or by passing it through a red hot tube. But when electric sparks are made to pass through it for a long time, its bulk is increased, as Dr Priestley first observed; and in that case, as Mongez discovered, an inflammable gas is always evolved. By 18 hours labour Mr Saussure junior produced an increase of  $\frac{1}{130}$  part of the whole; one-tenth of the carbonic acid had disappeared, and a quantity of carbonic oxide had been formed. The copper wires employed to transmit the sparks were oxidized at the expence of the acid, which was thus partially converted into carbonic oxide §.

Action of water. 4. Water absorbs it gradually when allowed to remain long in contact with it. The rapidity of the absorption, as Mr Lane first discovered, is much increased by agitation. At the temperature of 41° water absorbs its own bulk of this gas. The specific gravity of water saturated with it is 1.0015. This water, at the temperature of 35°, has little taste; but if it be left a

\* Bergman, i. 9-

† At least near the surface of the earth. Lamanon, Mongez, and the other unfortunate philosophers who accompanied La Perouse in his last voyage, have rendered it not improbable, that at great heights the quantity of this gas is much smaller. They could detect none in the atmosphere at the summit of the Peak of Teneriffe.—See Lamanon's Memoir at the end of La Perouse's Voyage.

& Phil. Mag. xiv. 359.

### CARBONIC

few hours in the temperature of 88°, it assumes an agreeable acidity, and a sparkling appearance \*.

Ice absorbs no carbonic acid; and if water containing it be frozen, the whole separates in the act of freezing +. This gas also separates from water at the boiling temperature 1.

By means of artificial pressure, the quantity of this gas absorbed and condensed by water is much increased. Some of the aerated alkaline water, prepared in Britain as a medicine, is said to contain about thrice its volume of carbonic acid gas §.

When this liquid carbonic acid is left exposed to the air in an open vessel, the acid soon makes its escape in the form of gas, and leaves the water in a state of purity. Bergman left a bottle filled with carbonic acid gas uncorked, and found that in a few days it contained nothing but common air.

5. Carbonic acid is not acted upon by oxygen, nor Action of is it altered by any of the simple combustibles, incombustibles, or metals. Charcoal indeed absorbs it, but it gives it out again unchanged. From the experiments of Rouppe and Van Noorden, it appears that this absorption is exceedingly rapid, provided the charcoal be sufficiently freed from air, by allowing it to cool from a red heat in a vacuum. They found that charcoal is capable of absorbing rather more than fourteen times its bulk of carbonic acid gas ¶. These experiments have been confirmed by others made in a different way by

simple bodies.

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Chap. II.

t Ibid. \* Bergman, i. 9. + Priestley, i. 120. & A very convenient apparatus for this purpose has been contrived by Mr Gilbert Austin, and described in the Irisb Transactions, viii. 131. I Ann. de Chim, XXXII. II.

Book II. Division II.

Count Morozzo\*. At a red heat charcoal converts is into carbonic oxide gas.

Phosphorus is insoluble in carbonic acid gas †; but phosphorus is capable of decomposing this acid by compound affinity, when assisted by a sufficient heat, as has been demonstrated by Tennant and Pearson. Iron also and zinc, and several other metals, are capable of producing the same effect, as has been discovered by Priestley and Cruikshanks. In the first case the phosphorus is partly acidified, partly combined with lime, and charcoal is deposited : in the second, the metals are oxidized, and the gaseous oxide of carbon evolved.

When carbonic acid is mixed with sulphureted, phosphareted, or carbureted hydrogen gas, it renders them less combustible, but produces no farther sensible change.

Carbonates.

6. This acid is capable of combining with alkalies, and with several of the earths and metallic oxides, and forms with them salts, distinguished by the name of *carbonates*. All the earthy carbonates are insoluble in water. Hence the reason that carbonic acid renders lime water, barytes water, and strontian water turbid. The earth held in solution in these waters combines rapidly with the carbonic acid, which is of course absorbed, if in the state of gas, while the carbonate formed precipitates slowly in the form of a white powder. This occasions the milkiness which immediately ensues. As carbonic acid is the only gas not instantaneously absorbable by water, which renders lime wa-

\* Nicholson's Journal, ix. 262.

+ Fourcroy and Vauquelin, Ibid. xxi. 205-

ter, or barytic or strontian water, turbid, its presence Chap. II. may be always ascertained by means of these liquids. As it is completely absorbed by them, it may be easily separated by them from other gases with which it may be mixed, and its quantity ascertained by the diminution of volume which the residuum of gas has undergone.

7. From the experiments of Saussure, it appears that carbonic acid scarcely combines with alumina\*.

Water containing a little soda, and supersaturated with carbonic acid, has been employed with much advantage under the name of aerated alkaline water, as a palliative in cases of urinary calculus.

8. The opinious of chemists concerning the composi- Composition of carbonic acid have undergone as many revolutions as its name. Dr Priestley and Bergman seem at first to have considered it as an element; and several celebrated chemists maintained that it was the acidify-Afterwards it was discovered to be a ing principle. compound, and that oxygen gas was one of its component parts. Upon this discovery the prevalent opinion of chemists was, that it consisted of oxygen and phlogiston ; and when hydrogen and phlogiston came (according to Mr Kirwan's theory) to signify the same thing, it was of course maintained that carbonic acid was composed of oxygen and hydrogen : and though Mr Lavoisier demonstrated, that it was formed by the combination of carbon and oxygen, this did not prevent the old theory from being maintained; because carbon was itself considered as a compound, into which a very

\* Jour. de Pbys. lii. 280

tion.

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great quantity of hydrogen entered. But after Mr Lavoisier had demonstrated, that the weight of the carbonic acid produced was precisely equal to the charcoal and oxygen employed; after Mr Cavendish had discovered that oxygen and hydrogen when combined did not form carbonic acid, but water-it was no longer possible to hesitate that this acid was composed of carbon and oxygen. Accordingly all farther dispute about it seems now at an end. At any rate, as we have already examined the objections that have been made to this conclusion, it would be improper to enter upon From the experiments of Mr Smithson them here. Tennant, compared with those of Lavoisier, and Messrs Allen and Pepys, we may consider carbonic acid as composed of about

> 28 carbon 72 oxygen

## 100

Decomposition. If any thing was still wanting to put this conclusion beyond the reach of doubt, it was to decompound carbonic acid, and thus to exhibit its component parts by analysis as well as synthesis. This has been actually done by the ingenious Mr Tennant. Into a tube of glass he introduced a bit of phesphorus and some carbonate of lime. He then sealed the tube hermetically, and applied heat. Phosphate of lime was formed, and a quantity of charcoal deposited. Now phosphate of lime is composed of phosphoric acid and lime; and phosphoric acid is composed of phosphorus and oxygen. The substances introduced into the tube were phosphorus, lime, and carbonic acid; and the substances found in it were phosphorus, lime, oxygen, and charcoal.

#### FLUORIC.

The carbonic acid, therefore, must have been decom- Chap. IL. posed, and it must have consisted of oxygen and charcoal. This experiment was repeated by Dr Pearson, who ascertained that the weight of the oxygen and charcoal were together equal to that of the carbonic acid which had been introduced : and in order to show that it was the carbonic acid which had been decomposed, he introduced pure lime and phosphorus; and instead of obtaining phosphate of lime and carbon, he got nothing but phosphuret of lime. These experiments\* were also confirmed by Messrs Fourcroy, Vauquelin, Sylvestre, and Broigniart +.

SECT. VI.

#### OF FLUORIC ACID.

THE mineral called fluor or fusible spar, and in this History. country Derbyshire spar, was not properly distinguished from other spars till Margraff published a dissertation on it in the Berlin Transactions for 1768. He first proved that it contained no sulphuric acid as had been formerly supposed ; he then attempted to decom-

\* Ann. de Chim. xiii. 312.

+ Count Mussin-Puschkin having boiled a solution of carbonate of potash on purified phosphorus, obtained charcoal. This he considered as an instance of the decomposition of carbonic acid, and as a confirmation of the experiments related in the text. See Ann. de Chim. XXV. 105.

Book II. Division II. pose it by mixing together equal quantities of this mineral and sulphuric acid, and distilling them. By this method he obtained a *white sublimate*, which he supposed to be the fluor itself volatilized by the acid. He observed with astonishment that the glass retort was corroded, and even pierced with holes. Nothing more was known concerning fluor till Scheele published his experiments three years after; by which he proved that it is composed chiefly of lime and a particular acid, which has been called *fluoric acid*.

It is always obtained from fluor spar, in which mineral it is found in abundance. For the investigation of the properties of this acid, we are indebted chiefly to Scheele and Priestley.

Preparation. 1. It may be obtained by putting a quantity of the spar in powder into a retort, pouring over it an equal quantity of sulphuric acid, and then applying a very gentle heat. A gas issues from the beak of the retort, which may be received in the usual manner in glass jars standing over mercury. This gas is *fluoric acid*\*.

The acid may be obtained dissolved in water by luting to the retort a receiver containing water. The distillation is to be conducted with a very moderate heat, not only to allow the gas to condense, but also to prevent the fluor itself from subliming. After the process, provided a glass retort has been employed, a crust of white earth is found in the receiver, which has all the properties of silica.

\* In order to obtain this acid pure, platinum or silver vessels ought to be employed; for the acid dissolves a portion of glass and even of leaden vessels.

## FLUORIC.

Scheele supposed that the silica produced was form- Chap. II. ed of fluoric acid and water; and Bergman adopted the same opinion. But Wiegleb and Bucholz showed that the quantity of silica was exactly equal to what the retort lost in weight; and Meyer completed the proof that it was derived from the glass, by the following experiment: He put into each of three equal cylindrical tin vessels a mixture of three ounces of sulphuric acid and one ounce of fluor, which had been pulverized in a mortar of metal. Into the first he put one ounce of pounded glass; into the second, the same quantity of quartz in powder; and into the third, nothing. Above each of the vessels he hung a sponge moistened with water; and having covered them, he exposed them to a moderate heat. The sponge in the first cylinder was covered with the crust in half an hour: the sponge in the second, in two hours; but no crust was formed in the third, though it was exposed several days. In consequence of this decisive experiment Bergman gave up his opinion, and wrote an account of Meyer's experiment to Morveau, who was employed in translating his works, to enable him to correct the mistake in his notes.

Soon after the discovery of this acid, difficulties and doubts concerning its existence as a peculiar acid were started by some French chemists, disguised under the name of Boulanger, and afterwards by Mr Achard and Mr Monnet. To remove these objections Mr Scheele instituted and published a new set of experiments; which not only completely established the peculiar nature of the fluoric acid, but once more displayed the unrivalled abilities of the illustrious discoverer \*. It

\* Scheele, ii. 38, and Crell's Annals, 1786, i. 3.

Book II. Division II. would be needless to enumerate these objections, as they originated entirely from want of precision, and did not produce a single convert.

Properties.

2. Fluoric acid gas is invisible and elastic like air; it does not maintain combustion, nor can animals breathe it without death. It has a pungent smell, not unlike that of muriatic acid. It is heavier than common air. It corrodes the skin almost instantly.

3. Neither caloric nor light produce any alteration on it.

Action of water. 4. When water is admitted in contact with this gas, " it absorbs it rapidly; and if the gas has been obtained by means of glass vessels, it deposits at the same time a quantity of silica.

Water absorbs a considerable proportion of this gas, but the precise quantity has not been determined. The compound is usually termed *fluoric acid* by chemists. It is specifically heavier than water, has an acid taste, reddens vegetable blues, and does not freeze till cooled down to  $23^{\circ}$ <sup>\*</sup>. When heated, the acid gas is easily expelled, except the last portions of it, which adhere with great obstinacy.

Of simple bodies. 5. Neither oxygen gas nor any of the simple combustibles or incombustibles produce any change on fluoric acid, either in the gaseous or liquid state.

6. Fluoric acid gas does not act upon any of the metals; but liquid fluoric acid is capable of oxidizing iron, zinc, copper, and arsenic. It does not act upon gold, platinum, silver, mercury, lead, tin, antimony, cobalt. 7. It combines with alkalies, earths, and metallic ox-

Fluates.

\* Priestley, ii. 361.

ides, and forms with them salts which are denominated Chap. II. fluates.

The most singular property of fluoric acid is the facility with which it corrodes glass and siliceous bodies, especially when hot, and the ease with which it holds silica in solution even when in the state of gas. This affinity for silica is so great, that the thickest glass vessels can only withstand its action for a short time; and the greatest precautions are scarcely sufficient to obtain it entirely free from siliceous earth.

s. It produces no change, as far as is known, upon any of the acids already described.

9. As fluoric acid produces an insoluble compound with lime, it may be employed with great advantage, as Pelletier has observed, to detect the presence of that earth when held in solution. A drop or two of the acid causes a milky cloud or precipitate to appear, if any lime be present. The property which this acid has Used for of corroding glass, has induced several ingenious men glass. to attempt, by means of it, to engrave, or rather etch upon glass. The glass is covered completely with wax ; and then that part where the letters or figures are to appear is laid bare by removing the wax. The whole is then exposed for some time to the hot vapours of fluoric acid. This simple process is employed with advantage in writing labels on glass vessels, and in graduating thermometers, and other similar instruments. The discovery is by no means new : It has been shown by Beckman and Accum, that this acid was employed for that purpose by Henry Swanhard, an artist of Nuremberg, as early as 1670. He seems to have kept his

etching on

## ACIÓ PRODÚCTS.

Book II. Division II.

Composition. art for some time secret ; but the receipt was made public by Pauli in 1725\*.

Till lately we were entirely ignorant of the constituents of this acid. Dr Henry tried in vain to decompose it by means of electricity; but Mr Davy's late attempts have been more successful. Potassium has the property of decomposing it, and the decomposition is attended with combustion †. A proof that oxygen is one of its constituents. The base of the acid is analogous to sulphur ‡. It combines with the potash formed, or with the potassium if there be an excess of that substance. It is combustible, and produces by its combustion fluoric acid. Hence it is obvious that this acid is truly an acid product. No name has hitherto been given to its peculiar basis.

\* See Beckman's History of Inventions, and Accum, Nicholson's Jourual. iv. 1.-The following advertisement, published by these gentlemen from a German publication of 1725, will give an idea of the method employed by that artist. " Take spiritus nitri per distillationem, put it into a retort, and apply a strong heat. When it has passed over into the receiver, throw into it some powdered green Bohemian emerald (which, when heated, shines in the dark), otherwise called besphorus. This being done, place the receiver, containing the mixture, on a heated sandbath for about four-and-twenty hours, and it will be fit for the purpose. To use this corrosive acid, take a pane of glass of any kind, clean it well, and free it from grease by washing with a ley; and when dry, trace out upon it, with sulphur and varnish, whatever you choose. Put a border of bees wax round it about one inch high, and then pour the corrosive acid, prepared as before directed, carefully over the whole surface of the glass, and let it stand undisturbed for some time; the longer the better. The glass will become corroded; and all you had traced before will now appear as if raised, or elevated, above the surface of the glass, in a very . distinct and pleasing manner." The hesphorus here mentioned was evidently fluor spar.

+ Phil. Mog. xxxiii. 89.

† Nicholson's Journal, xxii. 238.

BORACIC.

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## SECT. VII.

OF BORACIC ACID.

THE word boran first occurs in the works of Geber, History. an Arabian chemist of the 10th century. It is a name given to a species of white salt much used by various artists. Its use in soldering metals appears to have been known to Agricola.

Borax is found mixed with other substances in Thibet. It seems to exist in some lands adjacent to lakes. from which it is extracted by water, and deposited in those lakes; whence in summer, when the water is shallow, it is extracted and carried off in large lumps. Sometimes the water in these lakes is admitted into reservoirs; at the bottom of which, when the water is exhaled by the summer's heat, this salt is found. Hence it is carried to the East Indies, where it is in some measure purified and crystallized : in this state it comes to Europe, and is called tincal. In other parts of Thibet, it seems, by accounts received from China, they dig it out of the ground at the depth of about two yards. where they find it in smaller crystalline masses, called by the Chinese mi poun, boui poun, and pin pouin ; and the earth or ore is called pounxa \*.

Though borax has been in common use for nearly three centuries, it was only in 1702 that Homberg, by

\* Kirwan's Miner. ii. 37.

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Book II. Division II.

distilling a mixture of borax and green vitriol, discovered the boracic acid. He called it narcotic or sedative salt, from a notion of his that it possessed the properties indicated by these names. In his opinion, it was merely a product of the vitriol which he had used; but Lemery the Younger soon after discovered, that it could likewise be obtained from borax by means of the nitric and muriatic acids. Geoffroy afterwards discovered that borax contained soda; and at last Baron proved, by a number of experiments, that borax is composed of boracic acid and soda ; that it may be reproduced by combining these two substances; and that therefore the boracic acid is not formed during the decomposition of borax, as former chemists had imagined, but is a peculiar substance which pre-existed in that salt.

This conclusion has been called in question by Mr Cadet \*; who affirmed, that it was composed of soda, the vitrifiable earth of copper, another unknown metal, and muriatic acid. But this assertion has never been confirmed by a single proof. Mr Cadet has only proved, that boracic acid sometimes contains copper; and Baumé's experiments are sufficient to convince us, that this metal is merely accidentally present, and that it is probably derived from the vessels employed in crystallizing borax; that boracic acid generally contains a little of the acid employed to separate it from the soda with which it is combined in borax; and that crude borax contains a quantity of earth imperfectly saturated with boracic acid. All which may be very true; but they are altogether insufficient to prove that boracic acid is

\* Jour. de Phys. 1782.

not a peculiar substance, since it displays properties different from every other body.

Messrs Exschaquet and Struve \* have endeavoured, on the other hand, to prove, that the phosphoric and boracic acids are the same. But their experiments merely show, that these acids resemble one another in several particulars; and though they add considerably to our knowledge of the properties of the phosphoric acid, they are quite inadequate to establish the principle which these chemists had in view; since it is not sufficient to prove the identity of the two acids, to show us a resemblance in a few particulars, while they differ in many others. Boracic acid must therefore be considered as a distinct substance.

1. The easiest method of procuring boracic acid is Preparathe following one : Dissolve borax in hot water, and filter the solution; then add sulphuric acid, by little and little, till the liquid has a sensibly acid taste. Lay it aside to cool, and a great number of small shining laminated crystals will form. These are the boracic acid. They are to be washed with cold water, and drained upon brown paper.

2. Boracic acid, thus procured, is in the form of thin Properties. hexagonal scales, of a silvery whiteness, having some resemblance to spermaceti, and the same kind of greasy feel. It has a sourish taste at first +, then makes a bitterish cooling impression, and at last leaves an agreeable sweetness. It has no smell ; but when sulphuric acid

\* Jour. de Pbys. xxviii. 116.

+ Owing most probably to the remains of the acid employed in procuring it; for it loses that taste when heated to redness.

tion.

Chap. II.

Book II. is poured on it, a transient odour of musk is produ-Division II. ced \*.

> It reddens vegetable blues. Its specific gravity is 1.479 + while in the form of scales; after it has been fused it is 1.803 ‡.

> 3. It is not altered by light. It is perfectly fixed in the fire. At a red heat it melts, and is converted into a hard transparent glass; which becomes somewhat opaque when exposed to the air, but does not attract moisture.

> 4. It is much less soluble in water than any of the acids hitherto described. Boiling water scarcely dissolves 0.02 of boracic acid, and cold water a still smaller quantity. When this solution is distilled in close vessels, part of the acid evaporates along with the water, and crystallizes in the receiver. Water, therefore, renders it in some measure volatile, though it is perfectly fixed when in a state of dryness.

Of simple bodies.

Action of water,

> 5. Neither oxygen gas, the simple combustibles, the simple incombustibles, nor the metals, produce any change upon boracic acid, as far as is at present known.

> 6. It is soluble in alcohol; and alcohol containing it burns with a green flame. Paper dipped into a solution of boracic acid burns with a green flame.

> Though mixed with fine powder of charcoal, it is nevertheless capable of vitrification; and with soot it melts into a black bitumen-like mass, which is, however, soluble in water, and cannot be easily calcined to ashes, but sublimes in part §.

- \* Reuss, de Sale Sedat. 1778.
- 1 Hassenfratz, Ann. de Chim. xxviii. 11.

+ Kirwan's Min. ii, 4. § Keir's Dictionary.

## BORACIC.

With the assistance of a distilling heat, it dissolves in oils, especially in mineral oils; and with these it yields fluid and solid products, which give a green colour to spirit of wine.

When boracic acid is rubbed with phosphorus, it does not prevent its inflammation; but an earthy yellow matter is left behind \*.

It is hardly capable of oxidizing or dissolving any of the metals except iron and zinc, and perhaps copper.

Boracic acid combines with alkalies, alkaline earths, and alumina, and most of the metallic oxides, and forms compounds which are called *borates*.

The component parts of this acid were till lately unknown. Fabroni announced that he considers it as a modification of muriatic acid, and that it may be prepared from that acid; but he has not yet published the experiments upon which these opinions are founded  $\ddagger$ . A very curious set of experiments have been made on it by Crell. By digesting oxymuriatic acid on it for a very long time, he succeeded in decomposing it, and obtained from it a substance exactly resembling charcoal in its properties, and a volatile acid resembling the muriatic in the greater number of its properties, but differing from it in not precipitating lead from its solution  $\ddagger$ . Mr Davy has succeeded in decomposing this acid by means of potassium, and has shown that it is composed of oxygen, and a combustible basis of a black

\* Keir's Dictionary.

+ Fourcroy, ii. 128.

‡ Ann. de Chim. xxxv. 202.—Crell considers this volatile acid as very similar to the sebacic.

P

Vol. II.

Composi-

Book II. Division II. colour, which has a greater resemblance to charcoal than to any other substance \*. It becomes white, and is doubtless converted into boracic acid by exposure to the air.

\* Nicholson's Jour. xxii. 232

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### ACID SUPPORTERS.

The bilewing TABLE CINDIS a view of all the solid

pilore, their composition, and the proportion of

-A scertained.

Proportion of

Oxygen to 100 Base. CLASS IL. ACID SUPPORTERS.

THE acid supporters are distinguished by the follow- properties, ing properties:

1. They cannot be produced by combustion. Hence their base is either a simple incombustible or a metallic oxide.

2. They are capable of supporting combustion. Hence they readily acidify the combustible bases, and convert 

3. They are decomposed by exposure to a high temperature; their oxygen in that case making its escape in the state of a gas.

The only acids which possess these properties in perfection are those which have the simple incombustibles and arsenic for their bases; but from analogy I refer the whole of the metallic acids to this head: None of them can be produced by combustion; and as they contain a maximum of oxygen, they are of course incombustible : They cannot, therefore, be referred to any of the other two classes:

Chap. It.

Section 8

## ACID SUPPORTERS.

Book II. Division II. The following TABLE exhibits a view of all the acid supporters, their composition, and the proportion of their constituents, as far as they have been ascertained.

Number and composition.

Acids.	Bases.	Proportion of Oxygen to 100 Base.
Nitric Nitrous	Azote	236
Oxymuriatic Hyperoxymuriatic	Muriatic acid	29 194
Arsenic	Arsenic	53
Tungstic	Tungsten	25
Molybdic	Molybdenum	50
Chromic	Chromium	200
Columbic	Columbiam	

Some of these acids are of great importance in chemistry. This is chiefly owing to their activity: for which they are indebted to the state of the oxygen which they contain. The theory of Lavoisier applies with precision to this class of acids as well as to the first.

# SECT. I.

NITRIC.

## OF NITRIC ACID.

NITRIC ACID seems to have been first obtained in a History. separate state by Raymond Lully, who was born at Majorca in 1235. He procured it by distilling a mixture of nitre and clay. Basil Valentine, who lived in the 15th century, describes the process minutely, and calls the acid water of nitre. It was afterwards denominated aqua fortis and spirit of nitre. The name nitric acid was first given it in 1787 by the French chemists.

1. It is generally obtained in large manufactories by Preparadistilling a mixture of nitre and clay; but the acid procured by this process is weak and impure. Chemists generally prepare it by distilling three parts of nitre and one of sulphuric acid in a glass retort. This method was first used by Glauber. The neck of the retort must be luted into a receiver, from which there passes a glass tube into a bottle with two mouths, containing a little water, and furnished with a tube of safety\*. From the other mouth of this bottle there passes

\* A tube of safety is a tube open at its upper end, and having its lower end plunged in water. The water prevents any communication between the external air and the inside of the apparatus. If a vacuum happens to be formed within the vessels, the external air rushes down through the tube and prevents any injury to the vessels. On the other hand, if air is generated in the vessels, it forces the water up the tube, the height of which becomes thus the measure of the elasticity of the air in the vessels. By this contrivance the apparatus is in no danger of being broken, which otherwise might happen.

tion .

Chap. II.

Book II. Division II. a tube into a pneumatic apparatus to collect the gas which is evolved during the process. The apparatus is represented in fig. 12. The retort is to be heated gradually almost to redness. The nitric acid comes over and is condensed in the receiver, while the common air of the vessels, and a quantity of oxygen gas which is evolved, especially towards the end of the process, passes into the pneumatic apparatus, and the water in the bottles is impregnated with some acid which is not condensed in the receiver.

The acid, thus obtained, is of a yellow colour, and almost always contains muriatic and sulphuric acid, from , which it is difficult to free it completely. Perhaps the best way is to purify the nitre beforehand by repeated crystallizations, and by throwing down the muriatic acid that may adhere after all, by means of nitrate of silver. From the experiments of Lassone and Cornette, it appears that if nitric acid contaminated with muriatic be distilled with precaution, the whole of the muriatic acid comes over with the first portions, and the last portions are quite free from it \*. The common method is to mix impure nitric acid with nitrate of silver, to separate the precipitate, and re-distil. This method succeeds only when the acid is strong; if it be weak, a portion of muriatic acid still adheres to it. The sulphuric acid may be separated by rectifying the acid, by distilling it slowly, and withholding the last portions, or by distilling it 

After these foreign bodies are separated, the acid still retains a quantity of nitrous gas, to which it owes its

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\* Mem. Por. 1781, p. 645.

boud, if air is generation in the vessel

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## NITRIC.

colour and she red fumes which it exhales. This gas Chap II. may be expelled by the application of heat. Pure nitric acid remains behind, transparent and colourless, like water, of bouismodes of doid's has .22721 eew doidw

2. When newly prepared in this manner, it is a li- Properties. quid as transparent and colourless as water; but the affinity between its component parts is so weak, that the action of light is sufficient to drive off a part of its oxygen in the form of gas; and thus, by converting it partly into nitrous gas, to make it assume a yellow colour. Its taste is exceedingly acid and peculiar. It is very corrosive, and tinges the skin of a yellow colour, which does not disappear till the epidermis comes off. It is constantly emitting white fumes, which have an acrid and disagreeable odour. and fuoda to him to eno

3. It has a strong affinity for water, and has never yet Action of been obtained except mixed with that liquid. When concentrated, it attracts moisture from the atmosphere, but not so powerfully as sulphuric acid. It also produces heat when mixed with water, owing evidently to the concentration of the water 512 82:201 of istmonth

The specific gravity of the strongest nitric acid that can be procured is, according to Rouelle, 1.583; but at the temperature of 60°, Mr Kirwan could not procure it stronger than 1.5543. 10 erisq DOI ...... lo

But as this liquid acid is a compound of two ingre- Of the dients, namely, pure nitric acid and water, it becomes nitric acid. an object of the greatest consequence to ascertain the proportion of each of these parts. This problem has lately occupied the attention of Mr Kirwan, who has endeavoured to solve it in the following manner.

He dried a quantity of crystallized carbonate of soda in a red heat and dissolved it in water, in such a pro-

strength of

Book II. Division II. portion that 367 grains of the solution contained 50.05 of alkali. He saturated 367 grains of this solution with 147 grains of nitric acid, the specific gravity of which was 1.2754, and which he ascertained to contain 45.7 per cent. of acid, of the specific gravity 1.5543, chosen by him as a standard. The carbonic acid driven off amounted to 14 grains. On adding 939 grains of water, the specific gravity of the solution, at the temperature of 58.5°, was 1.0401. By comparing this with a solution of nitrate of soda, of the same density, precisely in the manner described formerly under sulphuric acid, he found, that the salt contained in it amounted to  $\frac{1}{16.901}$  of the whole. There was an excess of acid of about two grains. The weight of the whole was 1439 grains: The quantity of salt consequently was  $\frac{1439}{16901} = $5.142$  grains. The quantity of alkali was 50.05 - 14 = 36.05. The quantity of standard acid employed was 67.18; the whole of which amounted to 103.23 grains : but as only 85.142 grains entered into the composition of the salt, the remaining 18.088 must have been pure water mixed with the nitric acid. But if 67.18 of standard acid contain 18.088 of water, 100 parts of the same acid must contain 26.92\*.

One hundred parts of standard nitric acid, therefore, are composed of about 73.62 parts of pure nitric acid, and 26.38 of water. But as Mr Kirwan has not proved that nitrate of soda contains no water, perhaps the

\* Irish Trans. iv. I.

## NITRIC.

proportion of water may be greater. He has rendered it Chap II. probable, however, that nitrate of soda contains very little water.

Mr Kirwan's real acid, then, is nitric acid, of that degree of strength which enters into the composition of nitrate of soda. The proportion of this real acid, contained in nitric acid of different specific gravities, has been given by Mr Kirwan in the following TABLE :

NOT DESCRIPTION	14000	Here had a start of the	
1CO Parts	Real	100 Parts	Real
Sp. Gravity.	Acid.	Sp. Gravity.	Acid.
1.5543	73.54	1.3975	50.74
1.5295	69 86	1.3925	50.00
1.5183	69.12	1.3875	49.27
1.2070	68.39	1.3825	48.53
1.4957	67.65	1.3775	47.80
1.4844	66.92	1:3721	47.06
1.4731	66.18	1.3671	46.33
1.4719	65.45	1.3621	45.59
1.4707	64.71	1:3571	44.86+
1.4695	63.98+	1.3521	44.12
1.4683	63.24	1.3468	43.38
1.4671	62.51	1.3417	42.65
1.4640	61.77	1.3364	41.91
1.4611	61.03	1.3315	41.18
1.4582	60.30	1.3264	40.44
1.4553	59.56	1.3212	39.71
1.4524	58.83	1.3160	.38.97
1.4471	58.09	1.3108	38.34
1.4422	57.36	1.3056	37.50
1.4373	56.62	1.3004	36.77
1.4324	55.89	1.2911	36.03
1.4275	55.15	1.2812	35.30+
1.4222	54.12+	1.2795	34.56
1.4171	53.68	1.2779	33.82
1.4120	52.94	1.2687	-33.09
1.4069	52.21	1.2586	32.35 -
1.4018	51.47	1.2500	31.62
		1 2500	5104

## ACID SUPPORTERS.

Book II. Division II.

£		and the second second		
100 Parts	Real	100 Parts	Real	ubflocilit.
Sp. Gravity.	Acid.	Sp. Gravity.	Acid.	decionica.
				ar afatta
1.2464	30.88	1.1779	22.06	10.21
1 2419	30.15	1.1.1.0.4	21.32	2.012.7122
1.2374	29.41	1.1639	20.59	Segrere.
1.2291	29.68	1.1581	19.85	amina
1.2209	27.94	1.1524	19.12	
1.2180	27.21-	1.1421	18.48	
1.2152	26.47	1.1319	17.65+	9 1129-1
1.2033	25.74+	1.1284	16.91	
1.2015	25.00	1.1241	16.17	
1.1963	24.26	1.1165	15.44	
1.1911	23.53	1.1111	14.70	
1.1845	24.79	1.1040	13.27	

Mr Davy considers as pure acid the permanently elastic vapour or gas formed by saturating nitrous gas with oxygen gas. This gas is of a pale yellow colour, and a specific gravity 2.44 times that of air. It is not pure acid, containing undoubtedly a portion of nitrous gas. The following TABLE exhibits the proportion of this acid contained in nitric acid of different, densities, according to the experiments of that ingenious chemist \*.

					- UP	1.1.2	. 3
-	100 Parts Nitric acid, of Sp. Gr.	Tru	e acid.	1	Water.	0	• 1
		-	-	-		-	-
ł	1.5040	9	1.55	112	8.45	ġ	• [
	1.4475	18	0.30	185	19.61	4	-1
1	1.4285	17	1.65	100	28.35	4	• .[
1	1.3906	16	2.96	103	37.04	8	• 1
1	1.3551	15	6.88	4	13.12	8	• [
	1.3186	5	2.03	4	17.97	2	• :
1	1.3042	• 4	9.04	1.64	50.96		•1
	1.2831	- 4	6*03	1 3	53.97		· I
	1.2090	. 4.	5.27	1 2	54.73	1	• 2
	20	I	1		- 25		• [
-	1 A 4				31	CR.	- 5

\* Davy's Researches, p. 41.

4. When nitric acid is exposed to the action of heat, it boils at the temperature of  $248^{\circ}$ , and evaporates completely without alteration; but when made to pass through a red hot porcelain tube, it is decomposed, and converted into oxygen and azotic gas  $\ddagger$ . When cooled down to  $-66^{\circ}$ , it begins to congeal; and when agitated, it is converted into a mass of the consistence of butter  $\ddagger$ . But an account of the freezing points of this acid, as ascertained by Cavendish, has been already given in a preceding part of this Work  $\S$ . Lassone and Cornette have ascertained, that when weak nitric acid is boiled or distilled, the weakest portion comes first over-into the receiver; but when the acid is concentrated, the strongest portion comes first over  $\parallel$ .

5. Oxygen gas has no action whatever on nitric acid; but all the simple combustibles decompose it, unless we are to except the diamond. When poured upon sulphur or phosphorus ¶ at a high temperature, it sets them on fire; but at a moderate temperature it converts them slowly into acids, while nitrous gas is exhaled. It inflames charcoal also at a high temperature, and even at the common temperature, provided the charcoal be perfectly dry and minutely divided \*\*. Hydrogen gas produces no change on it at the temperature of the atmosphere; but when passed along with it through

Action of simple substances.

\* Bergman, ii. 142.

+ Fourcroy, ii. 82.

a de Chouis de l' Andersie de Dire

† Fourcroy and Vauquelin, Ann. de Chim. xxix. 282.

San B

§ Vol. 1. p. 523. Mem. Par. 1781, p. 645.

According to Brugnatelli, when a bit of phosphorus is wrapt up in paper, dipt in nitric acid, and struck smartl with a hammer upon an anvil, a detonation takes place. Jour. de Chim. iv. 113.—With me, howeyer, the experiment did not succeed. **\*\*** Proust. 235

Chap. II. Action of heat.

## ACID SUPPORTERS.

Book II. Division II. a red hot porcelain tube, it detonates with great violence; water is formed, and azotic gas evolved \*.

When this acid is poured upon oils, it sets them on This is occasioned by a decomposition both of fire. the acid and oil. The oxygen of the acid combines with the carbon and with the hydrogen of the oils, and at the same time lets out a quantity of caloric. Hence we see that the oxygen which enters into the composition of the nitric acid still contains a great deal of caloric; a fact which is confirmed by a great number of other phenomena. The combustion of oils by this acid was first taken notice of by Borrichius and Slare +; but it is probable that Homberg communicated it to Slare. In order to set fire to the fixed oils, it must be mixed with some sulphuric acid; the reason of which seems to be, that these oils contain water, which must be previously removed. The sulphuric acid combines with this water, and allows the nitric acid, or rather the oil and nitric acid together, to act. The drying oils do not require any sulphuric acid : they have been boiled, and consequently deprived of all moisture.

6. Azote has no action on nitric acid; but muriatic acid decomposes it by combining with a portion of its oxygen, nitrous gas and oxymuriatic gas being evolved. A mixture of nitric and muriatic acids was formerly called *aqua regia*; it is now known by the name of nitro-muriatic acid.

7. It is capable of oxidizing all the metals except gold, platinum ‡, and titanium. It appears, from the

\* Fourcroy, il. 82. † *Pbil. Trans.* Abr. ii. 653, and iii. 663. † Nitre, however, acts upon platinum, as Mr Tennant has proved. *Pbil. Trans.* 1797.—Morveau had made the same observation in the *Elimens de Chimie de l'* Academie de Dijon.

## NITRIC.

experiments of Scheffer, Bergman, Sage, and Tillet, Chap. II. that nitric acid is capable of dissolving (and consequently of oxidizing) a very minute quantity even of gold.

It even sets fire to zinc, bismuth, and tin, if it be poured on them in fusion, and to filings of iron if they be perfectly dry \*.

8. Nitric acid combines with alkalies, earths, and the oxides of metals, and forms compounds which are called nitrates.

9. Nitric acid absorbs nitrous gas with great avidity. assumes a yellow or brown colour, and the property of emitting dense yellow fumes. In this state it was formerly known by the name of phlogisticated nitric acid.

The liquid at present distinguished in most chemical books by the name of nitrous acid, is nothing else than this combination. Its nature was first investigated by Dr Priestley, who demonstrated, by very decisive experiments, that it is a compound of nitric acid and nitrous gas. This opinion was embraced, or rather it was first fully developed, by Morveau t. But the theory A comof Lavoisier, which supposed the difference between colourless and yellow nitric acid, to depend merely on the first containing a greater proportion of oxygen than the second, for some time drew the attention of chemists from the real nature of the combination. Raymond published a dissertation in 1796, to demonstrate the truth of the theory of Priestley and Morveau; and the same thing has been done still more lately by Messrs Thomson and Davy ‡.

pound of nitric acid and nitricoxide.

\* Proust, Dijon Academicians, and Cornette. + Encyc. Method. Chim. i. 18.

1 Davy's Researches, p. 30.

## ACID SUPPORTERS.

Book II. Division II. Nitric acid being capable of absorbing very different proportions of nitrous gas, it is evident that there must be a great variety of *nitrous acids*, to use the common phrase, differing from each other in the proportion of nitrous gas which they contain; unless we choose to confine the term to the compound formed by saturating nitric acid completely with nitrous gas.

When nitrous gas is placed in contact with nitric acid, the acid absorbs it slowly, and acquires first a pale yellow colour, then a bright yellow : When a considerable portion more of nitrous gas is absorbed, the acid becomes dark orange, then olive, which increases in intensity with the gas absorbed; then it becomes of a bright green; and lastly, when fully saturated, it becomes blue green. Its volume and its volatility also increase with the quantity of gas absorbed; and when fully saturated, it assumes the form of a dense vapour, of an exceedingly suffocating odour, and difficultly condensible by water. In this state of saturation it is distinguished by Dr Priestley by the name of nitrous acid vapour. It is of a dark red colour, and passes through water partly without being absorbed. The quantity of nitrous gas absorbed by nitric acid is very great. Dr Priestley found, that a quantity of acid, equal in bulk to four pennyweights of water, absorbed 130 ounce measures of gas without being saturated \*. The component parts of nitrous acid, of different colours and densities, may be seen in the following TABLE, drawn up by Mr Davy, from experiments made by him on purpose, with much precision +. angenod k

\* Priestley, i. 383.

+ Davy's Researches, p. 37.

NITRIC.

300 Parts.	Sp. Grav.	Component Parts.			Chap. II.
			Water.	Nitrous Gas.	Varieties
Solid nitric acid	1.504	91.55	8.45	ALLES SOLLS	
Yellow nitrous	1.502	90.5	8.3	2	, stear
Bright yellow .	1.500	88.94	8.10	2.96	e i i i i i
Dark orange	1.480	86.84	7.6	5.56	5 M 1 M
Light olive	1.479	86.00	7.55	6.45	
Dark olive	1.478	85.4	7.5	7.1	
Bright green	1.476	84.8	7.44	7.76	2 1
Blue green	1.475	84.6	7-4	8.00	

The colour of nitric acid depends, in some measure, also on the proportion of water which it contains. When to yellow nitric acid concentrated, a fourth part by weight of water is added, the colour is changed to a fine green; and when equal parts of water are added. it becomes blue \*. Dr Priestley observed, that water impregnated with this acid in the state of vapour became first blue, then green, and lastly yellow. A green nitric acid became orange-coloured while hot, and retained a yellow tinge when cold. A blue acid became vellow on being heated in a tube hermetically sealed. An orange-coloured acid, by long keeping, became green, and afterwards of a deep blue; and when exposed to air, resumed its original colour. When yellow nitric acid is exposed to heat, the nitrous gas is expelled, and nitrie acid remains behind. The gas, however, carries along with it a quantity of acid, especially if the acid be concentrated. But nitrous acid vapour is not altered in the least by exposure to heat +.

# Bergman.

† Fourcroy, ii. 95.

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Book II. Division If. Nitrous acid vapour is absorbed by sulphuric acid, but seemingly without producing any change; for when water is poured into the mixture, the heat produced expels it in the usual form of red fumes\*. The only singular circumstance attending this impregnation is, that it disposes the sulphuric acid to crystallize +. This fact, first observed by Dr Priestley in 1777‡, was afterwards confirmed by Mr Cornette.

It is absorbed also rapidly by nitric acid, which assumes the different colours which distinguish nitrous acid, according to the proportion which it imbibes.

10. Nitric acid is one of the most important instruments of analysis which the chemist possesses; nor is it of inferior consequence when considered in a political or commercial view, as it forms one of the most essential ingredients of gunpowder. Its nature and composition accordingly have long occupied the attention of

Composition.

\* Priestley, iii. 144.

100

#### + Ibid. p. 156.

t Bernhardt, however, relates, in 1765, that once, when he was distilling a mixture of ten pounds of nitre with an equal quantity of calcined vitriol, which he had put into a retort, to which he fitted an adopter between the retort and the receiver, which contained a quantity of water—he observed a considerable quantity of a white crystalline salt formed in the adopter, while the liquid acid passed as usual into the receiver. This salt was very volatile, smoked strongly when it was exposed to the air, and exhaled a red vapour; it burnt to a black coal wood, feathers, or linen, as sulphuric acid does; and where a piece of it fell, it evaporated in form of a blood-red vapour, till the whole of it disappeared: Half an ounce of these crystals dissolved in water with spurting and hissing, like that of a red hot iron dipped in water, and formed a green nitrous acid. Some of this salt being put into a bottle, which was not well stopped, entirely vanished. These crystals were evidently the same with Dr Priestley's. See Keir's Dictionary.

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## NITRIC:

philosophers. Let us endeavour to trace the various steps by which its component parts were discovered.

As nitre is often produced upon the surface of the earth, and never except in places which have a communication with atmospheric air, it was natural to suppose that air, or some part of the air, entered into the composition of nitric acid. Mayow having observed, that nitre and atmospherical air were both possessed of the property of giving a red colour to the blood, and that air was deprived of this property by combustion and respiration—concluded that nitre contained that part of the air which supported combustion, and was necessary for respiration.

Dr Hales, by applying heat to nitric acid, and what he called *Walton mineral*, obtained a quantity of air possessed of singular properties. When atmospherical air was let into the jar which contained it, a reddish turbid fume appeared, a quantity of air was absorbed, and the remainder became transparent again \*. Dr Priestley discovered, that this air could only be obtained from nitric acid; and therefore called it *nitrous air*. He found, that when this gas was mixed with oxygen gas, nitric acid was reproduced. Here, then, we find that oxygen is a part of the nitric acid, and consequently that Mayow's affirmation is verified.

Dr Priestley, however, explained this fact in a different manner. According to him, nitrous gas is composed of nitric acid and phlogiston. When oxygen is added, it separates this phlogiston, and the acid of course is precipitated. This hypothesis was adopted by Mac-

\* Veget. Statics, ii. 284.

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Book II. Division II. quer and Fontana; and these three philosophers endeavoured to support it with their usual ingenuity. But there was one difficulty which they were unable to surmount. When the two gases are mixed in proper proportions, almost the whole assumes the form of nitrie acid; and the small residuum ( $\frac{s}{14}$ th part), in all probability, or rather certainly, depends on some accidental impurity in the two gases. What then becomes of the oxygen and phlogiston? Dr Priestley supposed that they formed carbonic acid gas; but Mr Cavendish proved, that when proper precautions are taken, no such acid appears \*.

Dr Priestley had procured his nitrons gas by dissolving metals in nitric acid; during the solution of which a great deal of nitrous gas escapes. He supposed that nitrous gas contained phlogiston, because the metal was oxidized (and consequently, according to the then received theory, must have lost phlogiston) during its for-Mr Lavoisier proved, that this supposition mation. was ill founded, by the following celebrated experiment +. To 945 grains of nitric acid (specific gravity 1.316) he added 1104 grains of mercury. During the solution 273-234 cubic inches of nitrous gas were produced. He then distilled the salt (oxide of mercury) which had been formed to dryness. As soon as it became red hot it emitted oxygen gas, and continued todo so till almost the whole of the mercury was revived: The quantity of oxygen emitted was 257.742 cubic inches. All that had happened, therefore, during the solution of the mercury, was the separation of the acid

\* Bbil. Trans. 1784. + Mem. Par. 1776, p. 673-

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into two parts; nitrous gas, which flew off, and oxygen, which united with the metal.

Mr Lavoisier concluded, therefore, that the whole of the nitrous gas was derived from the nitric acid; that nitric acid is composed of oxygen and nitrous gas; and that the proportions are nearly 64 parts by weight of nitrous gas, and 36 of oxygen gas.

But there was one difficulty which Mr Lavoisier acknowledged he could not remove. The quantity of oxygen obtained by decomposing nitric acid was often much greater than what was necessary to saturate the nitrous gas. Mr De Morveau attempted to account for this; but without success\*. Nitrons gas itself was evidently a compound : but the difficulty was to discover the ingredients. Mr Lavoisier concluded, from an experiment made by decomposing nitre by means of charcoal, that it contained azote; and several of Dr Priestley's experiments led to the same result. But what was the other ingredient?

Mr Cavendish had observed, while he was making experiments on the composition of water, that some nitric acid was formed during the combustion of oxygen and hydrogen gas, and that its quantity was increased by adding a little azote to the two gases before the explosion. Hence he concluded, that the formation of the acid was owing to the accidental presence of azotic gas. To verify this conjecture, he passed electrical sparks through a quantity of common air inclosed in a glass tube : the air was diminished, and some nitric acid formed. He repeated the experiment, by mixing

> \* Encyc. Method. Chim. Acide Nitrique. O 2

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Book II. Division II. together oxygen and azotic gas; and found, that when they bore a certain proportion to each other they were totally convertible into nitric acid.

These experiments were immediately repeated by Messrs Van Marum and Van Troostwyk, and with nearly the same result.

Dr Priestley had observed several years before these experiments were made, that atmospherical air was diminished by the electric spark, and that during the diminution the infusion of turnsol became red; but he concluded merely that he had precipitated the acid of the air. Landriani, who thought, on the contrary, that carbonic acid gas was formed, enounced the alteration of lime-water by it as a proof of his opinion. It was to refute this notion that Mr Cavendish undertook his experiments.

It cannot be doubted, then, that nitrie acid is composed of azote and oxygen; consequently nitrous gas is also composed of the same ingredients. And as nitrous gas absorbs oxygen, even from common air, and forms with it nitrie acid, it is evident that nitrie acid contains more oxygen than nitrous gas. But it is exceedingly difficult to ascertain the exact proportions of the component parts of this acid. Lavoisier concluded, from his experiments on the decomposition of nitre by charcoal, that nitric acid is composed of one part of azote and four parts of oxygen \*. But Davy has shown that this decomposition is more complicated than had been supposed; and that Lavoisier's experiments by no means warrant the conclasion which he drew from

\* Mom. de Sav. Etrang. zi. 226.

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them \*. Cavendish, on the other hand, concluded from his experiments, that the acid which he formed, by combining together azote and oxygen by means of electricity, is composed of one part of azote and 2°36 of oxygen. With this result the late experiments of Mr Davy correspond very nearly. He formed his standard acid by combining together known quantities of nitrous gas and oxygen. Upon the whole, we may consider the proportion ascertained by Mr Cavendish as approaching the truth as nearly as possible. Nitric acid then is composed of 29°77 azote

70.23 oxygen

100.00

or nearly 1 part of azote to 2<sup>t</sup> of oxygen,

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### OF NITROUS ACID.

WHEN nitre, which is a compound of nitric acid and potash, is exposed to a red heat, it yields a considerable quantity of oxygen gas almost in a state of purity. If the process be conducted with the proper precautions and stopped in time, the nitre still retains the properties of a neutral salt. But the acid which it contains is obviously in a different state, since it has lost a considerable part of its oxygen. To this new state the term *aitrous acid* is applied.

\* Davy's Researches, p. 44.

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The experiment just recited was first made by Scheele, and mentioned in his dissertation on manganese, published in 1774 \*. He first pointed out the difference between nitric and nitrous acids, but confounded nitrous acid with nitric acid impregnated with nitrous gas. His opinions were adopted by Bergman, and modified by Lavoisier to suit his own theory. Notwithstanding the experiments of Priestley, which explained the nature of fuming nitric acid in a satisfactory manner, the opinion of Lavoisier and Scheele prevailed, and the term nitrous was applied to nitric acid whenever it was coloured with nitrous gas. Raymond drew the attention of chemists to the real constitution of fuming nitric acid in 1796, and the same thing was done more lately by Messrs Davy and Thomson. It is now generally allowed, that it is merely a combination of nitric acid and nitrous gas; and as such, its properties have been detailed in the preceding Section.

But the nitrous acid formed by exposing nitre to heat is undoubtedly a different substance, since nothing like the new salt can be formed by uniting potash to fuming nitric acid. But all the attempts to separate the nitrous acid from the potash have failed. When an acid, however weak, is applied, fumes of nitrous vapour are immediately disengaged. For any thing we know to the contrary, nitrous acid can exist only combined with a base. The genus of salts which it forms are called *nitrites*. They are obtained by exposing the nitrates to a graduated heat for a certain time, and then stopping the process. None of them have been hitherto examined with attention except the nitrite of potash.

\* Scheele's Opusc. i. 59.

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# OF OXYMURIATIC ACID. in powder. Place the report in the sand bath of a formory

THE composition of muriatic acid being imperfectly known, we may at present consider it as a simple substance. As it differs from all other acids in having the property of uniting with oxygen and forming a new set of acids which support combustion, it was thought preferable to separate it from the other acids, and to describe it along with azote, to which it bears a striking analogy. When united to oxygen, it forms the two acid supporters called oxymuriatic and byperoxymuriatic; the properties of which we shall examine in this and the succeeding Section.

Oxymuriatic acid was discovered by Scheele in 1774, History, during his experiments on manganese. He gave it the name of depblogisticated muriatic acid, from the supposition that it is muriatic acid deprived of phlogiston. The French chemists, after its composition had been ascertained, called it oxygenated muriatic acid; which unwieldy appellation Kirwan has happily contracted into oxymuriatic.

The properties of this acid pointed out by Scheele were so peculiar, that it immediately attracted attention. and the most distinguished chemists hastened with emulation to enter upon a field which promised so rich a harvest of discoveries. Bergman, Pelletier, Berthollet, Hermbstadt, Morveau, Fourcroy, Scopoli, Westrumb, &c. successfully examined its properties, and ascertained its

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Book II. Division II. action on other bodies; and more lately Mr Chenevix has published a most interesting dissertation on this acid and its combinations \*.

Preparation. 1. It may be procured by the following process: Put into a tubulated retort a mixture of three parts of common salt, and one part of the black oxide of manganese in powder. Place the retort in the sand bath of a furnace, plunge its beak into a small water trough, and lute a bent funnel into its mouth. When the mixture has acquired a moderate heat, pour into it at intervals through the bent funnel two parts of sulphuric acid, which ought to be somewhat diluted with water. An effervescence ensues, a yellow coloured gas issues from the retort, which may be received in large phials fitted with ground stoppers.

Properties.

2. Oxymuriatic acid gas is of a yellowish green colour. Its odour is intolerably acrid and suffocating. It cannot be breathed without proving fatal. The death of the ingenious and industrious Pelletier, whose chemical labours have been so useful to the world, was occasioned by his attempting to respire it. A consumption was the consequence of this attempt, which in a short time proved fatal. When atmospheric air containing a mixture of it is breathed, it occasions a violent and almost convulsive cough, attended with much pain in the chest. This cough usually continues to return at intervals for a day or two, and is accompanied with a copious expectoration.

3. It is capable of supporting combustion; in many cases even more capable than common air. When a

\* Phil. Trans. 1802.

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burning taper is plunged into it, the flame is diminish- Chap. II. ed, and acquires a very red colour ; a great quantity of smoke is emitted, and at the same time the taper consumes much more rapidly than in common air \*. The facility with which bodies take fire in this gas seems to depend on the ease with which it parts with its oxygen.

4. This gas is neither altered by exposure to light nor to caloric. It passes unaltered through red hot porcelain tubes +.

5. It does not unite readily with water. Scheele Action of found, that after standing 12 hours over water, 4ths of water. the gas were absorbed : the remainder was common air, which no doubt had been contained in the vessel before the operation. Berthollet surrounded several bottles containing it with ice: as soon as the water in these bottles was saturated, the gas became concrete, and sunk to the bottom of the vessels; but the smallest heat made it rise in bubbles, and endeavour to escape in the form of gas 1. Westrumb observed that it became solid when exposed in large vessels to the temperature of 40°; and that then it exhibited a kind of crystallization §. The specific gravity of water saturated with this gas, at the temperature of 43°, is 1.003 ||. From Berthollet's experiments, it appears that a cubic inch of water is capable of absorbing about 1.6 grains (French) of this acid gas. Water impregnated with this gas is usually distinguished by the name of oxymuriatic acid. It has a pale greenish yellow colour, and a suffocating

\* Fourcroy, Ann. de Chim. iv. 251. ‡ Jour. de Phys. 1785.

|| Berthollet, Ibid. 1785.

+ Fourcroy, ii. IIO. § Ibid. xxxvii. 382.

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### ACID SUFFORTERS.

Book II. Division II. odour like the gas; its taste is not acid, but astringent. It is usually prepared by causing the gas to pass thro' a succession of Wolle's bottles nearly filled with pure water. Light decomposes this acid, as Berthollet discovered, though it has no action on the gas.

6. It renders vegetable colours *white*, and not red, as other acids do; and the colour thus destroyed can neither be restored by acids nor alkalies. It has the same effects on yellow wax. If the quantity of vegetable colours to which it is applied be sufficiently great, it is found reduced to the state of common muriatic acid. Hence it is evident, that it destroys these colours by communicating oxygen. This property has rendered oxymuriatic acid a very important article in bleaching.

7. Oxymuriatic acid is not altered by oxygen gas; but all the simple combustibles are capable of decomposing it.

Action of simple combustibles, When one measure of hydrogen gas is mixed with two measures of oxymuriatic acid\*, and kept for 24 hours in a phial closed with a ground stopper, and the phial is then opened under water, the whole of the gaseous contents disappear. Hence it is obvious that they act upon each other: the hydrogen absorbs the oxygen of the acid, and is converted into water, while muriatic acid is evolved  $\ddagger$ . When a mixture of oxymuriatic acid gas and hydrogen gas is made to pass through a red hot porcelain tube, a violent detonation takes place  $\ddagger$ . By electricity a feeble explosion is produced.

This gas was obtained by a method to be described in the next Section, and obviously contained a portion of hyperoxymuriatic acid.

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- + Cruikshank's, Nicholson's Journal, 1802, v. 202.
- ‡ Fourcroy, ii. IIC.

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When melted sulphur is plunged into it, inflammation also takes place, and the sulphur is converted into sulphuric acid \*; but cold sulphur, though it is oxidized by this gas, does not take fire in it †,

When phosphorus is plunged into this gas, it immediately takes fire, burns with considerable splendour, and is converted into phosphoric acid. This was first described by an anonymous German writer ‡, and afterwards by Westrumb, Schmeisser, Fourcroy, and Vauquelin §.

When charcoal in fine powder is thrown into this gas, heated to about 90°, it also takes fire, according to Westrumb; but this experiment has not succeeded in the hands of other chemists. If we believe Professor Lampadius, the diamond also, when heated to redness, and plunged into oxymuriatic acid gas, burns in it with great splendour; but this experiment has also failed in the hands of other chemists.

Sulphureted, phosphureted, and carbureted hydrogen gas likewise decompose this acid; but none of them, except phosphureted hydrogen, produce spontaneous inflammation with it.

When one measure of carbureted hydrogen, from ether or camphor, is mixed with two measures of oxymuriatic gas, and allowed to remain for 24 hours in a phial closed with a ground stopper, the gases mutually decompose each other : water, muriatic acid, carbonic acid, and carbonic oxide, are formed. Accordingly,

\* Fourcroy, ii. 110.

† Westrumb, Crell's Annals, i. 150. Eng. Transl. See also Vol. I. p. 125, of this Work.

t Crell's Beitrage, vol. i. part 3. § Ann. de Chim. iv. 253.

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A ction o

Book II. Division II. when water is admitted, the whole is absorbed except about 0.43 of a measure: 0.09 of this residue is absorbed by lime-water; the rest is carbonic oxide. When there is an excess of oxymuriatic acid, the resulting substances are water, muriatic acid, and carbonic oxide \*. When a mixture of two parts oxymuriatic acid gas, and one part carbureted hydrogen, is fired by electricity, charcoal is deposited, and the gas diminished to 0.6 of a measure; 0.5 of which are absorbed by water, the rest is combustible  $\dagger$ .

8. Oxymuriatic acid is not acted upon by either of the simple incombustibles.

Action on metals.

9. Oxymuriatic acid oxidizes all the metals without the assistance of heat. Several of them even take fire as soon as they come into contact with the gas, as Westrumb first discovered. All that is necessary is to throw a quantity of the metal, reduced to a fine powder, into a vessel filled with the gas. The inflammation takes place immediately; the metal is oxidized, while the acid, decomposed and reduced to common muriatic acid, combines with the oxide, and forms a muriate. Arsenic burns in oxymuriatic acid gas with a blue and green flame; bismuth with a lively bluish flame; nickel, with a white flame, bordering on yellow; cobalt, with a white flame, approaching to blue; zinc, with a lively white flame; tin, with a feeble bluish flame; lead, with a sparkling white flame; copper and iron, with a red flame 1. Several of the metallic sulphurets, as cinnabar, realgar, sulphuret of antimony, take fire when thrown in powder into this gas.

‡ Jour. de Phys. xxxvii. 385.

<sup>•</sup> Cruikshanks, Nicholson's Journal, 1802, v. 204. † Id. Ibid.

# OXYMURIATIC.

10. When oxymuriatic acid gas and ammoniacal gas are mixed together, a rapid combustion, attended with a white flame, instantly takes place; both the gases are decomposed, water is formed, while azotic gas and muriatic acid are evolved \*. The same phenomena are apparent, though in a smaller degree, when liquid ammoniais poured into the acid gas t. The same decomposition takes place though both the acid and alkali be in. a liquid state. If four-fifths of a glass tube be filled with oxymuriatic acid, and the remaining fifth with ammonia. and the tube be then inverted over water, an effervescence ensues, and azotic gas is extricated ‡. It was by a similar experiment that Berthollet demonstrated the composition of ammonia.

11. This acid has not hitherto been combined with the alkalies, earths, or metallic oxides; nor have sufficient proofs been adduced that it is capable of combining with these bodies.

12. Oxymuriatic acid gas reddens nitrous gas, and converts it into nitrous acid. It produces no effect upon any of the acids hitherto described, except the sulphurous and phosphorous, which it converts into sulphuric and phosphoric.

13. When muriatic acid is mixed with nitric acid, Aquaregia, the compound has precisely the smell and the qualities of oxymuriatic. This mixture of the two acids was formerly called aqua regia ; but at present it is usually denominated nitro muriatic acid. It is first mentioned by Isaac Hollandus, and seems to have been known be-

\* Fourcroy, Ann. de Chim. iv. 255.

‡ Jour. de l'Ecole Polytechn,

Chap. IL. On ammonia.

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<sup>+</sup> Westrumb, Crell's Annales, i. 161. English Transl.

Book II. Division II. fore the muriatic acid itself. It was prepared by pouring nitric acid on common salt. The nitric acid decomposes the salt, and part of it unites with the muriatic acid thus set at liberty. As soon as these two acids are mixed they begin to act upon each other. The muriatic acid decomposes part of the nitric, combines with its oxygen, and is thus partly converted into oxymuriatic acid. Hence the suffocating odour of that acid which the mixture exhales. The nitrous gas, thus set at liberty, is absorbed by the undecomposed nitric acid, and converts it into nitrous acid. When these mutual combinations are completed, the action of the two acids on each other ceases. Thus nitro-muriatic acid is a mixture or combination of nitrous acid, muriatic acid, and oxymuriatic acid \*.

Supposed formation of muriatic acid. - Mr Lambe some time ago + announced, that when iron is acted upon by sulphureted hydrogen gas, a substance is produced which possesses all the properties of oxymuriate of iron (oxymuriatic acid combined with iron). In a solution of this gas in distilled water, he digested iron filings, previously purified by repeated washings with distilled water. The bottle was filled with the solution, and corked. The iron was presently acted upon; numerous bubbles arose, which drove the cork out of the bottle; they were strongly inflammable, and probably therefore pure hydrogen gas. The liquor gradually lost its odour of sulphureted hydrogen gas, and after some days smelled very much like stagnant rain-water. As the bubbles ceased to be produced, it recovered its transparency. On evaporating a small

\* Fourcroy, ii. 107. ‡ Manchester Mem. v. 194.

## OXYMURIATIC.

quantity of this solution in a watch-glass to dryness, a bitter deliquescent salt was left behind. On this salt a little sulphuric acid was dropped, and paper moistened with ammonia was held over the glass; white vapours were immediately formed over the glass; and consequently some volatile acid was separated by the sulphuric acid. Mr Lambe evaporated about eight ouncemeasures of the same liquor, and, as before, dropped a little sulphuric acid on the residuum ; a strong effervescence was excited, very pungent acid fumes arose, which, from their smell, were readily known to be muriatic. The same truth was established beyond a doubt, by holding a bit of paper, moistened with water, which made the vapours visible in the form of a grey smoke; a distinguishing characteristic, as Bergman has observed, of the muriatic acid. When manganese and mercury were dissolved in sulphureted hydrogen gas, the salts formed gave the same unequivocal marks of the presence of muriatic acid. and and a boniament doidw

This experiment of Mr Lambe has been lately repeated with every possible precaution by Vauquelin, and also by Guyton Morveau and Bouillon Lagrange; but these chemists did not succeed in obtaining a particle of oxymuriate of iron \*. We must conclude, then, that in the experiment of Mr Lambe, muriatic acid must have insinuated itself into his solution by some unknown channel. A fact mentioned by Berthollet may perhaps contribute something to explain this insinuation, and may also suggest a valuable hint towards the investigation of the real component parts of this ob-

\* Ann. de Chim. XXXVII. 191.

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Book II. Division II. stinate acid. He converted a quantity of iron into filings with all possible care. The filings, when washed with water, gave no marks of containing muriatic acid; but after being exposed for some days to the air, they furnished, when again washed, evident traces of the presence of muriatic acid \*.

Component parts of oxymuriatic acid. 14. From the action of oxymuriatic acid on combustibles, above described, and the compounds produced by it, no doubt can be entertained that it is a compound of muriatic acid and oxygen. This was first demonstrated by Berthollet, by a great number of ingenious and decisive experiments.

He attempted also to ascertain the proportion of its constituent parts. For this purpose he saturated 50 cubic inches (French) of water with oxymuriatic acid, and exposed the liquid for some days to the light of the sun. The oxygen gas disengaged amounted to 15 cubic inches (French) or 8 grains. The muriatic acid which remained in the liquid amounted to 65 grains. Hence it follows, that oxymuriatic acid is composed of 65 parts muriatic acid and 8 parts oxygen, or of about

89 muriatic acid

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But this method, though exceedingly simple and ingenious, was scarcely susceptible of precision. The analysis of Chenevix, made in a different way, deserves more confidence. This celebrated chemist caused a

\* Ann. de Chim. xxxvii. 194.—Similar facts had been pointed out long before by Margraff.

# OXYMURIATIC.

current of oxymuriatic acid gas to pass through a diluted solution of potash in water, till it contained an ex-He then evaporated to dryness, and process of acid. cured a saline mass containing all the potash, and the oxymuriatic acid. But when oxymuriatic acid is made to act upon potash in this manner, it divides itself into two portions; one portion consists of common muriatic acid, the other contains all the oxygen, and is therefore in the state of hyperoxymuriatic acid. The potash in the dry salt was therefore partly combined with muriatic acid, and partly with hyperoxymuriatic acid. Nitrate of silver precipitates the first of these acids from Hence an easy meall solutions, but not the second. thod of ascertaining the relative proportion of these two acids in a given quantity of salt presented itself. Accordingly Mr Chenevix ascertained, that in 100 parts of the dry salt, 84 consisted of 56.12 parts of potash combined with 27.88 of muriatic acid, and 16 of 3.8 of potash combined with 12.2 of hyperoxymuriatic acid. But he had ascertained, by a method to be described in the next section, that 12.2 parts of hyperoxymuriatic acid contained 9 parts of oxygen and 3.2 of muriatic acid. Therefore 27.88 + 3:2 = 31.08 muriatic acid ; and 9 parts of oxygen form 40.08 of oxymuriatic acid. Hence it follows, that oxymuriatic acid is composed of

77.5 muriatic acid

22.5 oxygen

is weight of

100 15. Though oxymutiatic acid has hitherto been placed among acids by chemists, it does not possess a single property which characterises that class of bodies. Its taste is not acid but astringent ; it does not convert ve-Vol. II. R

Not an acid,

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doubt by the ext

1. If a solution of

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Book] II. Division II. getable blues to red, but destroys them; it combines very sparingly with water, and is not capable of neutralizing alkalies, earths, or metallic oxides. It ought therefore to be placed among the oxides rather than the acids. But Scheele, the original discoverer of it, was induced, from the theory which then prevailed, to consider it as merely muriatic acid deprived of phlogiston; and after the mistake was discovered, the theory of Lavoisier respecting the acid principle, which then became fashionable, was considered as a sufficient reason for continuing it in its place among acids in spite of its properties. It must be confessed, however, that such arbitrary arrangements are no small impediments to the progress of the science.

# SECT. IV.

# OF HYPEROXYMURIATIC ACID.

THE existence of this acid was first suspected by Mr Berthollet, though he satisfied himself with little more than strong analogy. It has been lately put out of doubt by the experiments of Mr Chenevix.

Fermation.

1. If a solution of potash in six times its weight of water be put into a Wolfe's bottle, and a stream of oxymuriatic acid gas be made to pass through it in the usual way till the potash is saturated, crystals in the form of fine white scales are deposited in considerable quantity. These crystals have received the name of *byperoxygenized muriate of potasb.* They possess very

## HYPEROXYMURIATIC.

curious and important properties. If the liquid from which this salt is deposited be evaporated to dryness, another salt will be obtained, composed of muriatic acid and potash. These facts were all discovered by Berthollet. He concluded from them, that the oxymuriatic acid had been decomposed during the process ; that one portion of it lost the whole of its oxygen; and was reduced to the state of muriatic acid, while another portion combined with an additional dose of oxygen, and was converted into byperoxymuriatic acid. Hence the appellation of the salt which contained this last acid.

2. This theory of Berthollet was very plausible; and Opinion of it induced the greater number of chemists to believe that the substance to which hyperoxymuriate of potash. owes its peculiar properties, differs from oxymuriatic aacid by containing an additional dose of oxygen. But the opinion remained destitute of sufficient proof, till Mr Chenevix published his important dissertation on the subject in 1802. Mr Chenevix exposed 100 grains of hyperoxymuriate of potash to the heat of a lamp; it lost 2.5 parts of its weight, which he ascertained to be water. When heated to redness, a violent effervescence took place, and 112'5 cubic inches of oxygen gas, or 38.3 grains, were extricated. The salt which remained in the retort amounted to 53.5 grains, and five grains had been volatilized during the process \*. Hence it follows, that hyperoxymuriate of potash is composed of

Berthollet.

Confirmed by Chene

\* It had been long known that this saline residue is a compound of potash and muriatic acid.

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Ĉhap. II.

Book II. Division II. 2.5 water 38.3 oxygen 58.5 muriate of potash

and potano. Theat facts were all div

# thollet. He concluded from them 5'90

But Mr Chenevix ascertained, that the muriatic acid remaining in this saline residue amounted to 20 grains. Therefore 38.3 parts of oxygen, and 20 parts of muriatic acid, constitute 58.3 parts of the acid which exists in hyperoxymuriate of potash. That acid of course is composed of about.....66 oxygen

34 muriatic acid monthail T

# it induced the greater number of

The acid which constitutes a part of hyperoxymuriate of potash contains, we see, nearly nine times as much oxygen as exists in oxymuriatic acid. Thus the theory of Berthollet is confirmed in the fullest manner. We see that muriatic acid combines with two doses of oxygen; with the first dose it constitutes oxymuriatic acid, with the second the acid that exists in hyperoxymuriate of potash, which has been called *byperoxymuriatic* acid.

Oxymuriatic acid contains.....0.22 oxygen

remained in the retory amor

Hence it follows, that

Muriatic Oxymur.

acid Oxygen. acid. 1.00 + 0.29 = 1.29 Oxygen. Hyperoxymutiatic acid. 1.29 + 1.62 = 2.91 To become

Cannot be obtained scparate. 3. But though the peculiar nature of hyperoxymuriatic acid has been thus demonstrated, all attempts to procure it in a separate state have hitherto failed. Its properties therefore are but imperfectly known. From the amazing energy with which hyperoxymuriate of

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# HYPEROXYMURIATIC.

potash acts upon combustible bodies, it is obvious that Chap. If. it possesses in perfection the property of supporting combustion. It combines also with alkalies, earths, and metallic oxides, and forms salts of a very peculiar nature, which we shall afterwards examine. Mr Chenevix has rendered it probable, that it converts vegetable blues into red. It cannot be doubted that it combines with water. Several phenomena indicate, that when pure it assumes the gaseous state.

4. When sulphuric acid is poured upon hyperoxy- Action of genized muriate of potash, a violent decrepitation takes acid, place, and sometimes a flash of light is visible. The sulphuric acid in this case combines with the potash, and disengages the hyperoxymuriatic acid. This last acid rises in the state of a heavy vapour of a greenish yellow colour; its smell has some resemblance to that of nitrous gas, but peculiarly fetid : it is compared by Mr Chenevix to the odour emitted by brick kilns, mixed with that of nitrous gas. At the bottom of this vapour is a bright orange-coloured liquid, consisting of the sulphuric acid, the potash, and a portion of the hyperoxymuriatic acid. But the acid thus separated is not pure, being partly decomposed by the process, and being mixed with a portion of sulphuric acid. If we attempt to separate the hyperoxymuriatic acid by distillation, the moment the mixture is heated to about 120°, a violent explosion takes place, which breaks the vessels in pieces. This seems to be owing to the rapidity with which the acid is decomposed by a moderate heat \*. Nitric acid produces nearly the same effects as the sulphuric.

# Hoyle, Manchester Memoirs, v. 220.- Chenevix, Phil. Trans. 1802.

a's Joomal, 1983, 4 -

Book II. Division II. Of muriatic

5. When muriatic acid is poured upon the salt, a violent effervescence takes place, and gas is emitted abundantly, which has the smell and colour of oxymuriatic acid, but is much more rapidly absorbed by water. This process was first pointed out by Mr Cruikshanks. He obtained in this manner the gas which he employed in his experiments on carbonic oxide. When two measures of hydrogen gas are mixed with 2.3 measures of gas procured in this manner, Mr Cruikshanks found that the mixture explodes feebly with the electric spark, and is totally converted into water and muriatic acid. But two measures of hydrogen gas require one measure of oxygen gas to convert them into water. Hence Mr Cruikshanks infers, that 2.3 parts of the gas procured according to his process, contain one part of oxygen and 1.3 of muriatic acid; which gives as its component parts.....56.5 muriatic acid

43.5 oxygen

# 100:0\*

This shows us that the gas extricated from the salt by muriatic acid is not pure hyperoxymuriatic acid. Mr Chenevix supposes that it is a mixture of that acid and oxymuriatic acid gas: a portion of the first acid being decomposed by the muriatic acid, with which it comes in contact at the moment of its disengagement. But there are some reasons to question this opinion. When water, impregnated with oxymuriatic acid gas, obtained by Cruikshank's method, is mixed with liquid ammonia, scarcely any gas is extricated. The two bodies combine and form a salt.

\* Nicholson's Journal, 1802, v. 206.

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acid.

Much still remains to be done before the properties of this interesting acid be fully developed. Mr Chenevix has ascertained, that it is always formed when nitro-muriatic acid is boiled upon platinum, and likewse when oxide of titanium is precipitated by potash from muriatic acid.

# SECT. V.

# OF ARSENIC ACID.

ARSENIC, as we have seen formerly, is capable of combining with two doses of oxygen; and both the compounds which it forms with that body possess acid properties. The first, distinguished by Fourcroy by the name of arsenious acid, but more usually denominated white oxide of arsenic, has been already described\*. The second, called arsenic acid, was discovered by Scheele in 1775+, and its most remarkable properties investigated. Pelletier afterwards published a valuable dissertation on it. And more lately its properties and constituent parts have been more completely investigated by Proust and Bucholz 1.

1. Arsenic acid is usually prepared by the process Preparapointed out by Scheele. Three parts of white oxide of arsenic are dissolved in seven parts of muriatic acid, and the solution is mixed with five parts of nitric acid, and distilled to dryness. What remains is arsenic acid. But this method has been considerably improved by Bucholz. His method is as follows. Mix in a retort one

tion.

\* See Vol. I. p. 327. † Scheele, i. 129. ‡ Jour. de Chim. iv. 5.

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part of muriatic acid of the specific gravity 1.2, four
 parts of the white oxide of arsenic, and 12 parts of nitric acid of the specific gravity 1.25. Boil the mixture till the oxide disappear and nitrous gas ceases to be disengaged. Then evaporate to dryness, and expose the mass for a few minutes to a low red heat. What remains after this is solid arsenic acid.

Properties.

2. Arsenic acid, thus prepared, is a white solid mass, nearly tasteless. Its specific gravity is 3.391. It is very fixed. When heated strongly, it melts and remains transparent, and is converted into a glass, which acts powerfully on the vessel in which the experiment is performed. This glass attracts moisture from the air. When the heat is very strong, the acid gives out a little oxygen gas, and is at the same time partly converted into white oxide.

Action of wrater. 3. It dissolves very slowly in six parts of cold water; but two parts of boiling water dissolve it almost instantly, and it remains in a state of solution even tho' a considerable portion of that water be evaporated. With half its weight of water it has a syrupy consistency; and by farther evaporation it deposites crystals in grains \*. Its taste, when liquid, is acid, caustic, and metallic.

Of simple bodies. 4. Oxygen has no action whatever on this acid; neither is it affected by exposure to the open air.

5. The simple combustibles decompose it by the assistance of heat: And in these cases, as we learn from the experiments of Scheele and of the Dijon Academicians, combustion sometimes takes place; a proof that arsenic acid is a supporter of combustion.

\* Bucholz, Jour. de Chim. iv. 5-

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6. The simple incombustibles do not appear to pro- Chap. II. duce any alteration on it.

7. Several of the metals decompose it when assisted by heat. It does not act upon gold, platinum, silver, mercury. It oxidizes copper, iron, lead, tin, zinc, bismuth, antimony, cobalt, nickel, manganese, and arsenic, and in a strong heat mercury and silver.

8. It combines with alkalies, earths, and several of the metallic oxides, and forms compounds which have been called arseniates.

9. From the way in which this acid is formed, it Composicannot be doubted that it is composed of the white oxide of arsenic and oxygen. Nor is it very difficult to ascertain the proportion of these constituent parts; for the oxygen must be equivalent to the increase of weight which the oxide experiences during its acidification. From the experiments of Proust we learn, that this augmentation of weight amounts to 0.15 parts: Bucholz found it 0.16; a degree of coincidence as great as can be expected in experiments of that delicate nature. Hence it follows that arsenic acid is composed of about

86.5 white oxide of arsenic

13.5 oxygen rate in Thus, when preparty

# 100.0

But the oxide of arsenic contains nearly 0.25 of oxygen. This gives us arsenic acid composed of about

> 65 arsenic 35 oxygen L'ao nal sul of tanging in

It is only the second dose of oxygen, amounting to 13.5 parts, which gives this acid the property of sup-

mained of proceeding which, a001 a properties, have

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Book II. porting combustion, and of emitting oxygen gas when Division II. strongly heated.

# SECT. VI.

# OF TUNGSTIC ACID.

History.

THE substance called *tungstic acid* by Scheele and Bergman was discovered by Scheele in 1781. This philosopher obtained it from *tungstate of lime* by treating it with nitric acid and ammonia alternately. The acid dissolves the lime, and the ammonia combines with the tungstic acid. The ammoniacal solution, when saturated with nitric or muriatic acid, deposites a white powder, which is the *tungstic acid* of Scheele.

This powder has an acid taste, it reddens vegetable blues, and is soluble in 20 parts of boiling water. The De Luyarts have demonstrated, that this pretended acid is a compound of yellow oxide of tungsten, the alkali employed to dissolve it, and the acid used to precipitate it. Thus, when prepared according to the above described process, it is a compound of yellow oxide, ammonia, and nitric acid. Their conclusions have been more lately confirmed by the experiments of Vauquelin and Hecht. This substance must therefore be erased from the class of acids, and placed among the salts.

The real acid of tungsten is a yellow powder; the method of procuring which, and its properties, have been already described under the denomination of *yel*- tow oxide of tungsten\*. It ought rather, as Vauquelin and Hecht have properly remarked, to be classed among the oxides than the acids; for it is insoluble in water, tasteless, and has no effect on vegetable blues. It agrees with the acids indeed in the property of combining with alkalies and earths, and perhaps also with some metallic oxides, and forming with them salts, which have been denominated tungstates; but several other metallic oxides, those of lead, silver, and gold, for instance, possess the same property. These oxides therefore may be called acids with as much propriety as the yellow oxide of tungsten.

# SECT. VII.

# OF MOLYBDIC ACID.

MOLYBDIC acid was discovered by Scheele in 1778, History. during his experiments on the sulphuret of molybdenum, and its most remarkable properties ascertained. Scarcely any farther addition was made to our knowledge of it, till Mr Hatchett published his dissertation on the molybdate of lead, in the Philosophical Transactions for 1796. That ingenious chemist examined, with his usual precision, such of its properties as were connected with this subject. In the summer of 1805, an elaborate dissertation on molybdenum was published, in the 4th volume of Gehlen's Journal, by Bucholz,

\* Vol. I. p. 372-

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Book II. Division II. who did not neglect to ascertain the constituents and the mode of procuring this acid. To Scheele, Hatchett, and Bucholz, we owe most of the facts respecting molybdic acid at present known.

From the experiments of Bucholz it appears, that two of the combinations of molybdenum and oxygen are soluble in water; namely, the *blue oxide* and the *peroxide*. If the first be capable of neuralizing alkalies, it will belong to the class of acids, and may be distinguished by the name of *molybdous acid*; but its acid properties have not been ascertained. The peroxide, however, neutralizes alkalies. It has been always distinguished by the name of molybdic acid.

Preparation. It is usually prepared from molybdena, or native sulphuret of molybdenum, by the process pointed out by Scheele. Reduce the mineral to powder, and distil off it nitric acid, or rather a mixture of nitric and muriatic acids, till the whole is converted into a white mass. Edulcorate this mass with water to carry off the sulphuric acid formed, and the remains of the other acids. It is now molydic acid tolerably pure.

Another method has been lately pointed out by Bucholz. Reduce the mineral to a fine powder, and expose it to heat in an open crucible, stirring it with an iron rod till the whole assumes an ash-grey colour. The heat is to be at first a strong red, but gradually lowered as the roasting advances, to prevent the powder from cohering, which would render the completion of the process very difficult. By this roasting the sulphur is dissipated, and a considerable portion of the metal acidified. Reduce the mass to powder, and digest it a sufficient time in water holding soda or ammonia in solution; the molybdie acid is taken up, and combines with the alkali, while the impurities remain behind. Let the solution remain corked up till it has become clear, decant it off from the sediment if any thing has subsided, and pour into it some muriatic acid. The molybdic acid precipitates in the state of a fine white powder, and may be easily separated and edulcorated \*.

Molybdic acid, thus prepared, is a white powder, the Properties. specific gravity of which is 3.460. When heated in a close vessel it melts and crystallizes; but in an open vessel it sublimes in a white smoke, which attaches itself to cold bodies, and assumes the form of brilliant yellow scales.

It is soluble in 960 parts of boiling water. The solution is pale yellow; it has no taste, but reddens lit-The molybdic acid is precipitated from mus paper. this solution by sulphuric, nitric, and muriatic acids +.

Molybdic acid is not affected by oxygen gas; but it is decomposed by sulphur and charcoal, and several of the metals. When heated with the protoxide of molybdenum, the mixture is converted into blue oxide 1.

It combines with alkalies, earths, and several metallic oxides, and forms salts known by the name of molybdates.

Sulphuric acid dissolves molybdic acid when assisted by heat. The solution is colourless while hot; but when cold it assumes a deep blue colour, which is heightened by saturating the solution with soda. When this sulphuric acid solution is heated strongly, the sulphuric acid is evaporated, and molybdic acid remains. Muriatic acid also dissolves it. The solution is of a

\* Gehlen's Jour. iv. 604.

- + Hatchett, Phil. Trans. Ixxxvi. 323.
- t Bucholz, Gehlen, iv. 626.

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pale yellowish green colour; but it becomes blue when saturated with potash. Nitric acid does not dissolve this acid \*.

This acid, when combined with potash, forms a colourless salt.

Mixed with filings of tin and muriatic acid, it immediately becomes blue, and precipitates flakes of the same colour, which disappear after some time, if an excess of muriatic acid has been added, and the liquor assumes a brownish colour.

With the solution of nitrate of lead it forms a white precipitate, soluble in nitric acid.

When mixed with a little alcohol and nitric acid, it does not change its colour.

With a solution of nitrate of mercury, or of nitrate of silver, it gives a white flaky precipitate.

With the nitrate of copper it forms a greenish precipitate.

With solutions of sulphate of zinc, muriate of bismuth, muriate of antimony, nitrate of nickel, muriates of gold and platinum, it produces white precipitates when these solutions do not contain an excess of acid.

When melted with borax, it gives it a bluish colour.

Paper dipt in this acid becomes in the sun of a beautiful blue colour +.

From the experiments of Bucholz we learn, that when 100 grains of molybdenum are digested with nitric acid till they are converted into molybdic acid, and then dried, they now weigh about 149 grains. Hence it follows, that molybdic acid is composed of about 100

\* Hatchett, Phil. Trans. lxxxvi. 323. + Vauquelin, Phil. Mag. i. 282.

# CHROMIC.

parts metal and 49 oxygen; or very nearly two parts Chap. II. metal to one oxygen ; or per cent. of about

cine out it eaving anoth

67 molybdenum

33 oxygen Manua Vinsti, whom

100\*

# SECT. VIII. hear of the blowning, metry before the channel is in-

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# OF CHROMIC ACID. If it he then polverised, the powder is still neeple ; her

CHROMIC ACID, discovered lately by Vauquelin, has Preparaonly been found, in any quantity, in the red lead ore of Siberia, and in chromate of iron. Its properties have been investigated by Vauquelin and Mussin Puschkin.

It may be obtained by boiling the red lead ore with carbonate of soda, decanting off the fluid solution, and saturating it with one of the mineral acids; a red powder precipitates, which is chromic acid.

Chromic acid, thus obtained, is a red or orange-yel- Properties. low powder, of an acrid and strongly metallic taste. It is soluble in water, and crystallizes in the form of elongated prisms of a ruby colour.

When heated it gives out oxygen gas, and is converted into green oxide of chromium.

When mixed with filings of tin and the muriatic acid, it becomes at first yellowish brown, and afterwards assumes a beautiful green colour.

\* Gehlen's Jour. iv. 618.

Abriller assist

Book II. Division II. When mixed with a little alcohol and nitric acid, it immediately assumes a bluish green colour, which preserves the same shade even after desiccation. Ether alone gives it the same colour.

With a solution of nitrate of mercury, it gives a precipitate of a dark cinnabar colour.

With a solution of nitrate of silver, it gives a precipitate which, the moment it is formed, appears of a beautiful carmine colour, but becomes purple by exposure to the light. This combination, exposed to the heat of the blowpipe, melts before the charcoal is inflamed. It assumes a blackish and metallic appearance. If it be then pulverised, the powder is still purple; but after the blue flame of the lamp is brought in contact with this matter, it assumes a green colour, and the silver appears in globules disseminated throughout its substance.

With nitrate of copper, it gives a chesnut red precipitate. The head bet add publied we begind and the

With the solutions of sulphate of zinc, muriate of bismuth, muriate of antimony, nitrate of nickel, and muriate of platinum, it produces yellowish precipitates when these solutions do not contain excess of acid. With muriate of gold it produces a greenish precipitate.

When melted with borax or glass, it communicates to them a beautiful emerald green colour.

Paper impregnated with chromic acid assumes in the light a greenish colour.

When mixed with muriatic acid, the mixture is capable of dissolving gold like aqua regia: when this mixture of the two acids is distilled, oxymuriatic acid is disengaged, and the liquor assumes a very beautiful green colour.

## COLUMBIC.

Sulphuric acid, while cold, produces no effect upon Chap. II. it; but when warmed, it makes it assume a bluish green colour, probably by favouring the disengagement of oxygen.

When this acid is heated along with charcoal, it is reduced to the metal called chromium.

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# OF COLUMBIC ACID.

THIS metallic acid has hitherto been detected in one Preparaspecimen only, in which it is combined with the oxide tion. of iron. Mr Hatchett, to whom we owe the discovery of its peculiar properties, separated it from the iron by fusing it with potash. The alkali combined with a portion of the acid which was separated by water. Muriatic acid dissolved the oxide of iron thus deprived of its acid; and the ore, after this treatment, yielded an additional dose of acid when fused with potash. By repeating this process, the whole of the acid was combined with potash : the solution was limpid. Nitric acid precipitated the columbic acid from the potash in the state of white flakes.

1. The acid thus obtained is of a pure white colour, Properties. and not remarkably heavy. It has scarcely any taste. It is insoluble in water, but gives a red colour to paper stained with litmus. When exposed to a strong heat, it does not melt, but loses its lustre.

2. Sulphuric acid dissolves it, and forms a transparent colourless solution : But when the liquid is diluted. Vol. II. S

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Book II. Division II. with water, it becomes milky; a white precipitate falls, which becomes lavender blue; and when dry, brownish grey. It is semitransparent, and breaks with a vitreous fracture. This substance is a compound of sulphuric and columbic acids.

3. Nitric acid does not dissolve this acid; nor does it produce any change on its properties.

4. Muriatic acid dissolves it when assisted by heat. The solution does not become muddy when diluted with water. When evaporated to dryness, it leaves a pale yellow substance difficultly soluble in muriatic acid.

5. Potash and soda combine readily with columbic acid. With potash this acid forms a glittering scaly salt like boracic acid. It contains a slight excess of alkali; has an acrid disagreeable flavour; does not dissolve readily in cold water; but when dissolved, the solution is perfect and permanent. Nitric acid precipitates the columbic acid. But columbic acid is capable of expelling carbonic acid from potash \*.

The other properties of this acid remain to be investigated.

\* Hatchett, Phil. Trans. 1802.

CLASS III.

# COMBUSTIBLE ACIDS.

THE acids belonging to this class were formerly distinguished by the appellation of vegetable and animal acids. because almost the whole of them are procured from the animal and vegetable kingdom. They differ essentially from the other two classes of acids in several particulars.

1. If they be combined with potash and distilled, properties. they are completely decomposed, charcoal is usually evolved, and a considerable quantity of heavy inflammable air extricated ; whereas no combustible substance can be procured by exposing the other acids to heat \*.

2. All of them contain at least two simple combus+ tible substances as a base; whereas the others never contain more than one. These two substances are always carbon and bydrogen. Some of these acids contain likewise azote, over and above the two simple combustibles. Oxygen also usually enters into their composition in considerable quantity, but not perhaps always. To them, therefore, the theory of Lavoisier, respecting

# Sulphurous and phosphorous acids excepted, which emit sulphur and phosphureted hydrogen when exposed to heat.

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Divisible into four

orders.

the necessity of oxygen as the acidifying principle, does not strictly apply.

3. They do not seem capable of combining with different proportions of oxygen. Whenever the quantity of oxygen is changed, the proportion of the other constituents changes also. Of course the *termination* of their names ought not to indicate the proportion of oxygen which they contain; but should, if possible, be independent of that proportion altogether \*.

4. They are decomposed by the action of the more powerful acid supporters, and converted either into other combustible acids; or each of their constituents is saturated with oxygen, and converted into oxide and acid products.

5. The combustible acids may be very conveniently subdivided into four orders; which are distinguished from each other by the following properties:

The acids belonging to the first order are crystallizable, and they may be volatilized by heat without undergoing decomposition.

Those belonging to the second order are likewise crystallizable, but they cannot be volatilized without decomposition.

\* The French chemists who formed the new nomenclature were misled here. They made some of the names of the combustible acids end in *ic*, as if they were saturated with oxygen; and others in *ous*, as if they were capable of combining with an additional dose. The fact is, that none of them are, strictly speaking, saturated with oxygen; for all of them are capable of combining with *more*. But then they cannot combine with more without being totally decomposed, and converted into water, carbonic acid, &c. I have adopted the rule proposed by Mr Chenevix, which is calculated to avoid all ambiguity; the names of all the combustible acids are made to end in *ic*, and this without reference theory.

Those belonging to the third order are not crystallizable. Chap. II.

Under the fourth order are placed three acids, which, from the singularity of their properties ought to be separated from the rest. For want of a better name we shall distinguish them by the term *colorific*.

The following TABLE contains the names and component parts of all the acids belonging to each of these orders, as far as they have been ascertained.

# ORDER I. Crystallizable. Volatilizable.

Names.	Constituents.
1. Acetic 2. Benzoic 3. Sebacic 4. Succinic 5. Moroxylic 6. Camphoric 7. Oxalic ?	Carbon, hydrogen, oxygen.

# ORDER II. Crystallizable. Not volatilizable.

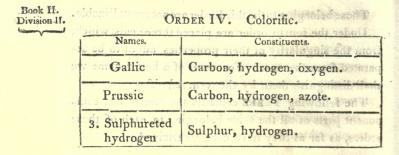
1. Mellitic 2. Tartaric 3. Citric 4. Kinic 5. Saclactic	Carbon, hydrogen, oxygen.
6. Uric	Carbon, hydrogen, azote, oxygen.
7. Laccic	Company within the state of the

# ORDER III. Not crystallizable.

1. Malic 2. Suberic 3. Formic	Carbon, hydrogen, oxygen.
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Table of the constituent parts.



We shall consider the properties of the acids belonging to the three first orders in the following Sections. The fourth order, for reasons to be assigned hereafter, will occupy a separate Chapter.

# SECT. I.

#### OF ACETIC ACID.

THIS acid is employed in three different states, which have been distinguished from each other by peculiar names. When first prepared, it is called *vinegar*; when purified by distillation, it assumes the name of distilled vinegar, usually called *acetous acid* by chemists; when concentrated as much as possible by peculiar processes, it is called *radical vinegar*, and by chemists *acetic acid*. It will be necessary to describe each of these states separately.

Vinegar.

1. Vinegar was known many ages before the discovery of any other acid, those only excepted which exist ready formed in vegetables. It is mentioned by Moses, and indeed seems to have been in common use

#### ACETIC.

among the Israelites and other eastern nations at a very early period. It is prepared from wine, from beer, ale, and other similar liquids. These are apt, as every one knows, to turn sour, unless they be kept very well corked. Now sour wine or beer is precisely the same with vinegar.

Boerhaave describes the following method of making vinegar, which is said to be still practised in different places.

Take two large oaken vats or hogsheads, and in each Preparaof these place a wooden grate or hurdle at the distance of a foot from the bottom. Set the vessel upright, and on the grate place a moderately close layer of green twigs of fresh cuttings of the vine. Then full up the vessel with the footstalks of grapes, commonly called the rape, to the top of the vessel, which must be left quite open.

Having thus prepared the two vessels, pour into them the wine to be converted into vinegar, so as to fill one of them quite up, and the other but half full. Leave them thus for twenty-four hours, and then fill up the half-filled vessel with liquor from that which is quite full. Four-and-twenty hours afterwards repeat the same operation; and thus go on, keeping the vessels alternately full and half full during every twenty-four hours till the vinegar be made. On the second or third day there will arise, in the half-filled vessel, a fermentative motion, accompanied with a sensible heat, which will gradually increase from day to day. On the contrary, the fermenting motion is almost imperceptible in the full vessel; and as the two vessels are alternately tull and half full, the fermentation is by that means, in

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tion.

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some measure, interrupted, and is only renewed every other day in each vessel.

When this motion appears to have entirely ceased, even in the half-filled vessel, it is a sign that the fermentation is finished; and therefore the vinegar is then to be put into casks close stopped, and kept in a cool place. The process in summer usually lasts fifteen days; in winter it lasts longer \*.

All that is necessary to convert wine or beer into vinegar is the contact of the external air, a temperature of 80°, and the presence of some substance to act as a ferment. But the theory of this operation belongs to the Second Part of this Work ; our business at present is, not to investigate the method of making vinegar, but to examine the properties of acetic acid.

Properties.

Vinegar is a liquid of a reddish or yellowish colour, a pleasant sour taste, and an agreeable odour. Its specific gravity varies from 1.0135 to 1.0251, and it differs also in its other properties according to the liquid from which it has been procured. It is very subject to decomposition; but Scheele discovered, that if it be made to boil for a few moments, it may be kept afterwards for a long time without alteration. Besides acetic acid and water, vinegar contains several other ingredients, such as mucilage, tartar, a colouring matter, and often also two or more vegetable acids. When distilled at a

\* An account of the mode of making vinegar in France, almost precisely the same with that given in the text, was published in the Philosophical Transactions for 1670, vol. v. p. 2002. The methods at present practised in France are described in the 3d Volume of the *Elemens de Cby*mie, published by the Dijon Academy, p. 6. Many still follow the process described in the text; others a different one.

#### ACETIC.

temperature not exceeding that of boiling water, till about two-thirds, or five-sixths at most, of it have passed over, all these mpurities are left behind, and the product is pure acid, diluted with water. The residuum is still an acid liquid, and often lets fall crystals of tartar.

2. The acid thus obtained is a liquid as transparent Acetous and colourless as water, of a strong acid taste and an agreeable odour, somewhat different from that of vinegar. In this state it is usually called acetous acid or distilled vinegar.

It may be preserved without alteration in close vessels. When exposed to a moderate heat, it evaporates completely and without undergoing any change in its properties. When exposed to the action of cold, part of it congeals. The frozen portion, which consists almost entirely of water, may be easily separated; and by this method the acid may be obtained in a high degree of concentration. The more concentrated the acid is, the greater is the cold necessary to produce congelation. Mr Lowitz has ascertained that the acid itself, how much soever it be concentrated, crystallizes or congeals at the temperature of -22°.

3. When acetate of copper, reduced to powder, is put into a retort and distilled, there comes over a liquid at cetic acid. first nearly colourless and almost insipid, and afterwards a highly concentrated acid. The distillation is to be continued till the bottom of the retort is red hot. What remains in it then is only a powder of the colour of copper. The acid product, which should be received in a vessel by itself, is tinged green by a little copper which passes along with it; but when distilled over again in a gentle heat, it is obtained perfectly colourless

Preparation of a-

acid

Book II. Division II. and transparent. The acid thus obtained is exceedingly pungent and concentrated. It was formerly distinguished by the names of *radical vinegar* and *vinegar* of Venus.

This process was known to the alchymists, and had often been repeated by chemical philosophers; but the product was considered as merely highly concentrated acetous acid, till Berthollet published his experiments on it in 1785 \*. That skilful philosopher affirmed, that it differs from acetous acid in taste and smell, in its affinities for other bodies, and in the compounds which it forms with them. When it is obtained from acetate of copper by distillation, the powder which remains in the retort consists chiefly of copper in the metallic state. Hence he supposed, that the acetic acid gave out phlogiston to the copper, and received from it oxygen. When the existence of phlogiston was disproved, this theory was a little altered. It was concluded, that during the distillation, the acetic acid deprived the oxide of copper of its oxygen, and combined with it; and that radical vinegar therefore is acetous acid combined with a new dose of oxygen. For this reason it received the name of acetic acid.

This theory was generally admitted by chemists, till Mr Adet published his experiments on acetic acid in 1797<sup>†</sup>. He observed, that when acetate of copper is distilled, the products are not only acetic acid and water, but likewise carbonic acid and carbureted hydrogen gas; and that the residuum consists of copper and charcoal. He found that acetous acid did not absorb

\* Mem. Par. 1783.

1 Ann. de Clim. X2VII. 299-

#### ACETIC.

oxygen when distilled off black oxide of manganese, and that acetic and acetous acids have exactly the same effect upon metals. From these and some other similar experiments, he concluded that acetic and acetous acids do not differ from each other except in concentration.

This conclusion was considered as hasty, as he did not attempt to account for the very striking difference in the taste and smell of these acids, as he had neither repeated nor refuted the experiments of Berthollet. on which the opinion of the difference between these two acids was founded. The conclusion of Adet was opposed in 1798 by Chaptal, who published a set of experiments on the same subject\*. This philosopher endeavoured to demonstrate, as Berthollet had done before him, that acetic and acetous acids, even when of the same strength, possess different properties, and have different effects on other bodies. From the effect of sulphuric acid upon each, and from the quantity of charcoal which remains in the retort when equal quantities of each saturated with potash are distilled, he concluded that acetous acid contains a smaller proportion of carbon than acetic acid. And this he considered as the cause of the difference in their properties.

In 1800 a new set of experiments on the same subject was published by Mr Dabit of Nantes +. This chemist endeavoured to prove that acetic acid contains a greater proportion of oxygen than acetous. When he distilled a mixture of acetate of potash and sulphuric acid, the product was acetic acid; but when he substituted muriatic acid for sulphuric, he obtained acetous

\* Ann. de Chim. xxviii. 113. 1 Ibid. xxxviii. 66.

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Book II. Division II. acid; but when to this last mixture a little black oxide of manganese was added, he assures us that he obtained acetic acid. And in none of these cases was there any carbonic acid emitted till towards the end of the distillation.

Proved to be the same.

The experiments of Darracq have at last finally settled this dispute, by demonstrating that acetous and acetic acids differ merely in concentration. This able chemist repeated the experiments of Adet, which he found perfectly accurate, and performed several new ones; all of which left no doubt that acetous and acetic acids contain precisely the same proportion of oxygen. He next tried the opinion of Chaptal respecting the proportion of carbon in each. When equal quantities of acetic and acetous acids are combined with potash or soda, the dry salts distilled leave the same quantity of charcoal, and yield the same quantity of other products. When reduced to the same specific gravity, the two acids form precisely the same salts with all alkaline and earthy bases. Finally, acetous acid gradually becomes acetic acid when distilled repeatedly off dry muriate of lime; and in this case no gaseous body whatever is evolved. From these facts, it is impossible to entertain a doubt that the two substances are essentially the same, and that these apparent differences are owing to the great quantity of water with which acetous acid is diluted, and the mucilaginous matter which it still retains\*.

The same results were obtained also by Proust, who had drawn the same conclusions before he came ac-

\* Darracq, Ann. de Chim. xli. 264.

quainted with Darracq's paper \*. Henceforth the term acetous acid must either be wholly dropt by chemists, or employed in a sense different from what was formerly affixed to it.

4. This acid is transparent and colourless like water. Properties. It has a peculiar aromatic smell when in the state of acetous acid ; but concentrated acetic acid, when procured in the usual way, has an empyreumatic odour mixed with the natural smell of vinegar, owing to a small portion of oil formed during the process +.

Another method of procuring this acid in a concentrated state, has been proposed by different chemists. and brought to a state of perfection by Lowitz of Petersburgh. Distil a mixture of three parts of acetate of potash and four parts of sulphuric acid, till the acetic acid has come over into the receiver. To separate the sulphuric acid with which it is in some measure contaminated, rectify the liquid by distilling it off a portion of acetate of barytes. The acid that comes over crystallizes in the receiver.

The specific gravity of distilled vinegar varies from 1.007 to 1.0095; but radical vinegar is much more concentrated, its specific gravity being as high as 1.080 ‡. In that state it is extremely pungent and acrid; and when it is applied to the skin, it reddens and corrodes it in a very short time. It is exceedingly volatile; and when heated in the open air, takes fire so readily, that one would be tempted to suspect the presence of ether in it. It unites with water in any pro-

\* Jour. de Phys. lvi. 210. + Ann. de Chim. XXXVII. ILL. Richter. Gehlen's Jour. iv. II.

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Book II. Division II. portion; and when concentrated, the mixture evolves a good deal of heat.

5. Courtenvaux had long ago observed, that the last portions of acetic acid, which come over during the distillation, were susceptible of crystallizing in a moderate cold. Lowitz proposed a very ingenious method to obtain this acid in the state of crystals. He makes distilled vinegar into a paste with well burnt charcoal, and exposes the mixture to a heat not above 212°. The watery part is driven off, and the acid remains. A stronger heat drives off the acid itself in a very concentrated state. By repeating this process it may be obtained in crystals. The process of that chemist, detailed above, is more recent, and in every respect preferable.

Action of simple bodies. 6. Neither oxygen gas nor air have any very marked action on this acid: nor do the simple combustibles or incombustibles alter it at the common temperature of the atmosphere.

7. It is capable of oxidizing iron, zinc, copper, nickel, tin. It does not act upon gold, silver, platinum, mercury, bismuth, cobalt, antimony, arsenic. Its action on tellurium, tungsten, molybdenum, uranium, titanium, and chromium, has not been tried.

8. It combines with alkalies, earths, and metallic oxides, and forms compounds known by the name of *acetates*.

9. It is decomposed by sulphuric and nitric acids. The action of the other acids on it has scarcely been examined. <sup>1</sup>It dissolves boracic acid, and absorbs carbonic acid.

10. It has the property of combining with a great

number of vegetable bodies, such as oils, mucilage, and aromatics.

11. When nitric acid is made to act on this acid, it Composiconverts it into water and carbonic acid. When acetic acid, combined with a fixed alkali or earth, is exposed to a strong heat, it is almost completely decomposed; water, carbonic acid, and carbureted hydrogen gas, are emitted, and the base remains mixed with a quantity of charcoal. From these facts it follows, that it is composed of carbon, hydrogen, and oxygen, into which all these products may be ultimately resolved. But the proportion of these ingredients has not been ascertained with precision.

By distilling 7680 grains of acetate of potash, Dr Higgens obtained the following products \*:

Potash	3862.994 grains
Carbonic acid gas	1473.564
Carbureted hydrogen gas	1047.6018
Residuum, consisting of charcoal	78.0000
Oil	180.0000
Water	. 340.0000
Deficiency †	726.9402

This deficiency Dr Higgins found to be owing to a quantity of water and oil which is carried off by the elastic fluids, and afterwards deposited by them. He calculated it, in the present case, at 700 grains of water

\* Higgins on Acetous Acid, p. 26.

+ For 29'I grains of oxygen gas had also disappeared from the air of the vessels.

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tion.

Book II. Division II. and 26.9402 grains of oil. Now, since acetate of potash is composed of acetic acid and potash, and since the whole of the potash remained unaltered, it follows, that the acid was converted into carbonic acid gas, carbureted hydrogen gas, carbon, oil, and water; all of which are composed of oxygen, hydrogen, and carbon.

Now 1473.564 grains of carbonic acid gas are composed of 1060.966 grains of oxygen and 415.598 grains of carbon.

1047.6018 grains of carbureted hydrogen gas, from a comparison of the experiments of Dr Higgins and Lavoisier, may be supposed to consist of about 714.6008 grains of carbon and 333.0010 of hydrogen.

200.9402 grains of oil contain 163.4828 grains of carbon and 43.4574 grains of hydrogen.

1040 grains of water contain 884 grains of oxygen and 156 grains of hydrogen.

Therefore 3817.006 grains of acetic acid are composed of 1944.966 -29.1= 1915.866 grains of oxygen, 532.4584 grains of hydrogen, and 1368.6816 grains of carbon. Consequently 100 parts of acetic acid are composed of

> 50°19 oxygen 13°94 hydrogen 35°87 carbon

#### 100.00

These numbers can only be considered as very imperfect approximations to the truth; for the object of Dr Higgins was not to ascertain the proportions of the ingredients which compose acetic acid; and therefore his experiments were not conducted with that rigid accuracy which would have been necessary for that pur-

#### BENZOIC.

pose. Mr Proust endeavoured to prove that azote likewise is a component part of acetic acid; an opinion which had been entertained by Lavoisier. But when Trommsdorf repeated the experiments of Proust, which consisted in distilling different acetates, he obtained no traces either of ammonia or of prussic acid, as had been announced by the chemist of Madrid. Hence he concludes that acetic acid contains no azote, and that Proust's experiments must have been made upon impure acid \*.

# SECT. II.

BETTY AT LEADENSES FRAME THAT

# OF BENZOIC ACID.

BENZOIN, or BENJAMIN as it is sometimes called, is a History. kind of resin brought from the East Indies; obtained, according to Dr Dryander, from the styrax benzoe, a tree which grows in the island of Sumatra. This substance consists partly of a peculiar acid, described as long ago as 1608 by Blaise de Vigenere, in his Treatise on fire and salt, under the name of flowers of benzoin, because it was obtained by sublimation ; but it is now denominated benzoic acid.

1. The usual method of obtaining this acid is to put Preparaa quantity of benzoin, coarsely powdered, into an earth- tion. en pot, to cover the mouth of the pot with a cone of

\* Ann. de Chim. lviii. 190. T

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Book II. Division II. thick paper, and then to apply a very moderate sand heat. The benzoic acid is sublimed, and attaches itself to the paper. This method was tedious and difficult ; it being hardly possible to prevent the heat from scorching the benzoin, and volatilizing some empyreumatic oil, which soils and injures the acid sublimed. Neuman proposed moistening the benzoin with alcohol, and distilling it in a retort with a low heat. The acid comes over immediately after the alcohol, partly in crystals and partly of the consistence of butter \*. Geof. froy ascertained, in 1738, that this acid may be obtained by digesting benzoin in hot water. A portion is taken up, which is deposited in crystals as the water cools. Scheele published a different method in 1775; which being easier and more productive than any of the preceding, is usually preferred. This process is as follows + : Upon four parts of unslacked lime pour twelve parts of water, and after the ebullition is over add 96 parts more of water ; then put 12 parts of finely pounded benzoin into a tinned pan ; pour upon it first about six parts of the above milk of lime, mix them well together, and thus successively add the rest of the mixture of lime and water. If it be poured in all at once, the benzoin, instead of mixing with it, will coagnlate, and run together into a mass. This mixture ought to be boiled over a gentle fire for half an hour with constant agitation; then take it from the fire, let it stand quiet for an hour, in order that it may settle ; pour off the supernatant limpid liquor into a glass vessel. Upon the remainder in the pan pour 96 parts of pure water;

\* Neuman's Chemistry, p. 294.

+ Scheele, i. #24.

boil them together for half an hour, then take it from the fire, and let it settle; add the supernatent liquor to the former; pour upon the residuum some more water, boil it as aforesaid, and repeat the same process once more. At last put all the residuums upon a filter, and pour hot water several times upon it. During this process, the calcareous earth combines with the acid of benzoin, and separates it from the resinous particles of this substance. A small quantity of the resin is dissolved by the lime-water, whence it acquires a yellow colour. All these clear yellow leys and decoctions are to be mixed together, and boiled down to 24 parts, which are then to be strained into another glass vessel.

After they are grown cold, muriatic acid is to be added, with constant stirring, till there be no farther precipitation, or till the mass taste a little sourish. The benzoic acid, which was before held in solution by the lime, precipitates in the form of a fine powder.

Mr Hatchett has observed, that when benzoin is digested in sulphuric acid, a great quantity of beautifully crystallized benzoic acid is sublimed. This process is the simplest of all, and yields the acid in a state of purity; it claims therefore the attention of manufacturers \*.

2. Benzoic acid, thus obtained, is a fine light whitish Properties. powder, which is not brittle, but has rather a kind of ductility. Its taste is acrid, hot, and somewhat bitter. Its odour is slight, but peculiar and aromatic t. Its

. \* Hatchett's Additional Experiments on Tannin. Phil. Trant. 1805.

+ This odour is owing to a small portion of aromatic oil which adheres to the acid. It has been obtained without any smell by Giese, See Phil. Mog. xiv. 331.

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specific gravity is 0.667 ‡. It hardly affects the infusion of violets, but it reddens that of turnsol, especially when hot ||.

Heat volatilizes this acid, and makes it give out a strong odour, which excites coughing. When exposed to the heat of the blowpipe in a silver spoon, it melts, becomes as fluid as water, and evaporates without taking fire. It only burns when in contact with flame, and then it leaves no residuum behind. When thrown upon burning coals, it rises in a white smoke. When allowed to cool after being melted, it hardens, and a radiated crust forms on its surface ¶. When distilled in close vessels, the greater part of it sublimes unaltered, but some of it is decomposed. This portion is converted almost entirely into oil and carbureted hydrogen gas.

3. This acid is not altered by exposure to the air. Cold water dissolves no sensible quantity of it; but it is soluble enough in hot water : 480 grains of boiling water dissolves 20 grains of it; 19 of these are deposited, when the water cools in long, slender, flat, feather-like crystals \*.

Action of simple bobies.

4. It is not affected by oxygen gas, nor by any of the simple combustibles or incombustibles. It does not seem capable of oxidizing any of the metals +.

5. It combines with alkalies, earths, and metallic oxides, and forms salts known by the name of benzoates.

6. Concentrated sulphuric acid dissolves it without

"Harehott's Additiona

a Phil. May ave 335.

t Hassenfratz, Ann. de Chim. xxviii. II.

|| Morveau, Encyc. Method. Chim. i. 44.

I Lichtenstein. + Trommsdorf. \* Ibid.

heat, or any other change, except becoming somewhat Chap. II. brown : when water is poured into the solution, the benzoic acid separates, and coagulates on the surface without any alteration \*. Nitric acid presents precisely the same phenomena, as does also the sulphurous acid. Neither the muriatic, the oxymuriatic, nor the phosphoric acids dissolve it. Acetic acid, when hot, dissolves it precisely as water does ; but it crystallizes again when the acid cools +.

7. Alcohol dissolves it copiously, and lets it fall on the addition of water 1. Boiling alcohol takes up its own weight §.

This acid is sometimes used as a medicine, but much less frequently than formerly. tillation of talloy

The experiments of this chemist were

th and all the observations of the French

tert ained similar re-

# SECT. III.

# OF SEBACIC ACID.

CHEMISTS had long suspected that an acid could be History. obtained from tallow, on account of the acrid nature of the fumes which it emits at a high temperature ; but it was M. Grutzmacher who first treated of it particularly, in a dissertation De Ossium Medulla, published in 1748 ||. Mr Rhades mentioned it in 1753; Segner published a dissertation on it in 1754; and Crell exami-

\* Lichtenstein. f Id. . 1 Id. § Wenzel's Verwandt-Lconhardi. echaft, p: 302.

Book II. Division II.

ned its properties very fully in two dissertations published in the Philosphical Transactions for 1780 and 1782. It was called at first acid of fat, and afterwards sebacic acid.

But at the period when these chemists made their experiments, the characteristic properties of the different acids were not sufficiently known to enable them to distinguish acids from each other with precision, Thenard examined the subject in 1801, tried all the processes of Crell and Guyton Morveau, and found that the acids procured by them were either acetic or the acid employed in the process. Real sebacic acid had hitherto escaped the examination of chemists. Thenard found, however, that a peculiar acid was formed during the distillation of tallow. To it he consigned the appellation of sebacic acid. The experiments of this chemist were repeated in 1804 by Mr Rose, who obtained similar results, and confirmed all the observations of the French philosopher \*. The subject has lately been resumed by Mr Berzelius, who in an elaborate dissertation, published in 1806, has shown that the sebacic acid of Thenard bears a close resemblance to benzoic acid +, Indeed he considers it as nothing else than benzoic acid. contaminated with some unknown substance derived from the fat, which alters some of its properties, but from which it may be nearly freed by proper precautions.

Prepara-

1. The method of procuring sebacic acid pointed out by Thenard is as follows : Distil hog's lard, wash the product with hot water, separate this water, and drop into

\* Gehlen's Jour. iii. 170.

+ Ibid. 2d Series, ii. 275.

# SEBACIC.

it acetate of lead. A flaky precipitate appears, which is Chap. II. to be washed and dried, mixed with sulphuric acid, and heated. A melted substance, analogous to fat, swims on the surface, which is to be carefully separated. This substance is sebacic acid. It may be dissolved in hot water, and on cooling crystalline needles are deposited. This acid may be obtained also by evaporating the water employed in washing the product of distilled hog's lard. Or this water may be saturated with potash, and afterwards precipitated with acetate of lead as above \*.

During the distillation there comes over abundance of gas, which appears to be a mixture of carbonic acid and carbureted hydrogen. Into the receiver there drops a yellow-coloured water, impregnated with acetic acid, but containing no sebacic acid. It may, therefore, be put aside. But a much greater portion of oily matter passes over of the consistence of butter. The whole sebacic acid is contained in this matter, and may be separated by boiling it in water and evaporating the watery solution. The sebacic acid falls down in the state of small crystals. From the experiments of Mr Rose, we learn that the quantity of sebacic acid formed by this process is extremely small; a pound of hog's lard vielding little more than 40 grains, and tallow or suct still less +.

2. Sebacic acid is white ; it has no smell ; its taste Properties. is a pleasant sour, leaving in the mouth a very slight impression of bitterness. It reddens the infusion of turnsol. When heated it melts like tallow: on cooling it concretes into a crystalline mass. By a sudden and

\* Ann. de Chim. XXXIX. 194.

+ Gehlen, iii. 171.

Book II. Division IL violent heat it is decomposed. Berzelius has shown that it may be volatilized without decomposition, but that it requires a higher temperature for this purpose than benzoic acid.

Cold water dissolves but little sebacic acid, but boiling water takes up one-fourth of its weight. It separates as the water cools in small crystals. The crystals are needles; but by proper precautions it may be procured in long, large, and very brilliant plates. Alcohol dissolves it copiously, and so do the fixed and volatile oils \*. In all these respects, as Berzelius has shown, it agrees with benzoic acid.

It occasions a precibitate in the acetate and nitrate of lead, the nitrate of silver, the acetate and nitrate of mercury. It forms peculiar salts with the alkalies and earths. It does not render lime-water, barytes, or strontian water, turbid. Sebate of potash has little taste. does not attract moisture from the air ; and when sulphuric, nitric, or muriatic acid is poured upon it, sebacic acid is deposited : when its solution is concentrated and mixed with any one of these acids it becomes solid. Berzelius has shown, that in these properties also sebacic and benzoic acid agree with each other. He has compared the different salts which each of these acids forms with the respective bases, and shown that they also nearly agree in their properties. Benzoic acid is usually combined with some extractive matter, from which it is nearly as difficult to free it as it is to free sebacic acid from the substances with which it is united. In short, from the experiments of Berzelius, there can

\* Thenard and Rose, Ibid.

#### SUCCINIC.

be no doubt that the two acids, if not absolutely the Chap. If. same, at least approach very nearly to each other.

# SECT. IV.

# OF SUCCINIC ACID.

AMBER is a well-known brown, transparent, inflammable body, pretty hard, and susceptible of polish, found at some depth in the earth, and on the sea-coast of several countries. It was in high estimation among the ancients both as an ornament and a medicine.—When this substance is distilled, a volatile salt is obtained, which is mentioned by Agricola under the name of *salt* of amber; but its nature was long unknown. Boyle was the first who discovered that it was an acid \*. From *succinum*, the Laun name of amber, this acid has received the appellation of *succinic acid*.

Mr Pott seems to have been the first chemist who made a set of experiments to ascertain its properties, and who demonstrated that it differs from every other  $\dagger$ .

1. It is obtained by the following process: Fill a retort half-way with powdered amber, and cover the powder with a quantity of dry sand; lute on a receiver, and distil in a sand-bath without employing too much heat. There passes over first an insipid phlegm; then

Preparation.

\* Boyle abridged by Shaw, iii. 369.

† Mem. Berlin, 1753. See an abstract of his paper in Lewis's edition of Neuman's Chemistry, p. 237. 297

CINCLEMENTS

Book H. Division II. a weak acid, which, according to Scheele, is the acetic \*; then the succinic acid attaches itself to the neck of the retort; and if the distillation be continued, there comes over at last a thick brown oil, which has an acid taste.

The succinic acid is at first mixed with a quantity of oil. It may be made tolerably pure by dissolving it in hot water, and putting upon the filter a little cotton, previously moistened with oil of amber: this substance retains most of the oil, and allows the solution to pass clear. The acid is then to be crystallized by a gentle evaporation; and this process is to be repeated till the acid be sufficiently pure. Guyton Morveau has shown that it may be made quite pure by distilling off it a sufficient quantity of nitric acid, taking care not to employ a heat strong enough to sublime the succinic acid  $\ddagger$ .

Properties.

2. The crystals of succinic acid are transparent, white, shining, and of a foliated, triangular, prismatic form: they have an acid taste, but are not corrosive: they redden tincture of turnsol, but have little effect on that of violets.

They sublime when exposed to a considerable heat, but not at the heat of a water-bath. In a sand-bath they melt, and then sublime and condense in the upper part of the vessel; but the coal which remains shows that they are partly decomposed  $\ddagger$ .

3. One part of this acid dissolves in 96 parts of water at the temperature of 50°, according to Spielman §; in 24 parts at the temperature of  $52^{\circ}$ ; and in 2 parts of water at the temperature of  $212^{\circ}$ , according to Stock-

\* Bergman's Notes on Scheffer. ‡ Pott. † Ann. de Chim. xxix. 165. § Inst. Chem. § xii.

#### SUCCINIC.

ar de Neuforn\*; but the greatest part crystallizes as the water cools. According to Roux, however, it still retains more of the acid than cold water is capable of dissolving  $\dagger$ .

Two hundred and forty grains of boiling alcohol dissolve 177 of this acid; but crystals again shoot as the solution cools ‡.

4. Sulphuric acid dissolves it with the assistance of heat; but does not appear to decompose it. The same remark applies to nitric acid. Muriatic acid has but little action on it while cold; but when heat is applied, the whole coagulates into the consistence of a jelly §.

5. The compounds which this acid forms with alkalies, acids, and metallic oxides, have received the name of *succinates*.

6. When combined with soda, it crystallizes in four and six sided prisms. When this salt is distilled in a retort, the succinic acid is completely decomposed. There passes over into the receiver an acid liquor, which is the acetic much diluted, and a quantity of brown oil. At the same time carbonic acid gas and carbureted hydrogen gas are disengaged, and their remain in the retort soda and charcoal ||. Hence it follows, that this acid, like the others of the same class, is decomposed by heat, and that it is composed of oxygen, hydrogen, and carbon.

\* De Succino. † Morveau, Encys. Method. Chim. i. 72. ' t Wenzel's Verwandtschaft, p. 305. § Pott. Morveau. Ann. de Chim. xxix. 165.

# combustible Acids,

the water coals. According to Reary Lowerier, it still

Book II. Division II.

# territor is the soil than cold water is capable of SECT. V. SECT. V. TO SECT. Two building alcohol dis-

# OF MOROXYLIC ACID.

History.

A BOUT the year 1802, Dr Thompson observed a saline exudation on the bark of the morus alba, or white mulberry tree, growing in the botanical garden of Palermo in Sicily. It coated the bark of the tree in small grains of a yellowish and blackish brown colour. A quantity of this matter was collected and sent to Mr Klaproth, who published an analysis of it in 1803\*.

t gloop notigios

It has a taste resembling that of succinic acid; and when placed upon burning coals, it emits a vapour which irritates the organs of smell. In water it dissolves sparingly, forming a reddish-brown liquid, which yields by evaporation small needleform crystals, of the colour of pale wood, not deliquescing in the air. By dissolving these crystals in water, and treating them with various reagents, Klaproth ascertained them to be formed of lime united to a peculiar acid, which he called moroxylic, because the salt containing it was a production of the wood of the mulberry tree.

The salt dissolves but sparingly in water; hot water, taking up only 0.035, and cold 0.015 of it. From the solution the alkaline carbonates precipitate lime; but barytes causes no precipitate; a proof of the absence of

\* Scherer's Journal der Clemie, No. 55. p. 1. But I use the translation of the paper published in Nicholson's Journal, vii. 129.

sulphuric acid. It precipitates powerfully the solutions of silver, mercury, copper, iron, cobalt, and uranium, in nitric acid; and of lead and iron in acetic acid. Barytes water, acetate of barytes, muriate of tin, muriate of gold, and nitrate of nickel, produce scarcely any effect.

To obtain the acid, the solution of the salt was treated with acetate of lead. Forty-five grains of the precipitate thus obtained were mixed with 20 grains of sulphuric acid diluted with 60 grains of water. The sulphate of lead formed remained in the state of a white powder, while the moroxylic acid was dissolved and obtained by evaporation in the state of fine needles of the colour of pale wood.

The acid thus obtained has the taste of succinic acid: it is not altered by exposure to the air: it dissolves readily in water and in alcohol: it does not precipitate the metallic solutions like its salt.

When heated in a retort, a little acid liquor first comes over, which has the taste of the concrete acid: next, the acid rises unaltered, and adheres to the top and neck of the retort in colourless and transparent prismatic crystals. A coaly residuum remains in the vessel. Hence it appears, that a gentle sublimation is the best mode of obtaining this acid in a state of purity.

When the calcareous salt of moroxylate of lime is distilled, a quantity of inflammable air mixed with carbonic acid is obtained, and an acid liquor comes over, on which swims a brown oil. There remains in the retort a spongy mass of a pale brown colour, consisting of carbonate of lime mixed with some charry matter. From these phenomena it appears, that this acid, like the rest, is composed of oxygen, hydrogen, and carbon,

Properties.

Book II. Division II.

though the proportion of the constituents is unknown. The compounds which it forms with alkalies have received the name of *moroxylates*.

Such are the properties of this substance ascertained by Klaproth. The small quantity of the salt which he possessed prevented a more complete examination.

# SECT. VI.

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## OF CAMPHORIC ACID.

History.

CAMPHOR is a well-known white crystalline substance, of a strong taste and smell, obtained from a species of laurel in the East Indies. It is so volatile that it cannot be melted in open vessels, and so inflammable that it burns even on the surface of water.

When camphor is set on fire in contact with oxygen gas, it burns with a very brilliant flame; much calorie is disengaged, water is formed, the inner surface of the vessel is covered with a black matter, which is undoubtedly charcoal, and a quantity of carbonic acid gas is also produced \*. Hence it follows, that it is composed of hydrogen and carbon, at least principally.

Mr Kosegarten, by distilling nitric acid off camphor eight times successively, obtained an acid in crystals †, to which the name of *camphoric acid* has been given.

Preparation. 1. His experiments have been repeated by Mr Bouil-

<sup>\*</sup> Bouillon La Grange, Ann. de Chim. xxiii. 153. + Kosegarten de Campbora, &c. 1785.

#### CAMPHORIC.

lon La Grange. The process for obtaining camphoric Chap. II. acid, as described by this chemist, is as follows: Put into a retort one part of camphor and eight parts of nitric acid, of the specific gravity 1.33. Distil with a sand heat. A great deal of nitrous gas and carbonic acid gas is emitted, and a little camphor sublimes. This process must be repeated three times on the same camphor; so that 24 parts in all of nitric acid are neces-After the third distillation, when the retort is sary. allowed to cool, a number of crystals make their appearance in it. These are campboric acid. They amount to somewhat less than the half of the camphor employed.

2. Camphoric acid thus obtained is in snow-white Properties. crystals, of the form of parallelopipedons \*. These crystals effloresce in the air +.

Camphoric acid has a slightly acid bitter taste, and a smell like that of saffron.

It reddens vegetable colours.

3. It is soluble in 200 parts of cold water, according to Kosegarten; in 96 parts of water at the temperature of 60°, according to Bouillon La Grange. Boiling water dissolves Tth of its weight t.

According to Kosegarten, it is insoluble in alcohol; according to Bouillon La Grange, alcohol dissolves it; and when the solution is left in contact with the air of the atmosphere, the acid crystallizes. It is not precipitated from its solution in alcohol by the addition of water §.

\* Kosegarten de Campbora, &c. 1785. + La Grange. ‡ Kosegarten. § Bouillon La Grange, Ann. de Chim. xxvii, 40.

Book II. Division II.

Action of heat.

4. When this acid is placed on ignited coals, it emits a dense aromatic fume, and is entirely dissipated. By a gentler heat it melts, and is sublimed. If it be put into a heated porcelain tube, and oxygen gas be passed through it, the acid does not undergo any change, but is sublimed.

By mere distillation it first melts, and then sublimes; by which process its properties are in some respect changed. It no longer reddens the tincture of turnsol, but acquires a strong aromatic smell; its taste becomes less penetrating, and it is no longer soluble either in water or the sulphuric and muriatic acids. Heated nitric acid turns it yellow and dissolves it. Alcohol likewise dissolves it: and if this solution be left in contact with the air of the atmosphere, it crystallizes.

5. Camphoric acid does not produce any change on sulphur; alcohol and the mineral acids totally dissolve it; and so likewise do the volatile and the fat oils.

Camphoric acid does not precipitate lime from limewater. It produces no change on the solution of indigo in sulphuric acid.

6. It forms combinations with the alkalies, earths, and metallic oxides, which are called *campborates*.

# SECT. VII.

#### OF OXALIC ACID.

History.

WHEN nitric acid is poured upon sugar, and a moderate heat applied, the sugar soon melts, an effervescence

ensues, a great quantity of nitrous gas and carbonic acid gas is emitted; and when the effervescence ceases, and the liquid in the retort is allowed to cool, a number of small transparent crystals appear in it. These crystals constitute a peculiar acid, which has received the name of oxalic acid, because it exists ready formed, as Scheele has proved, in the oxalis acetosella, or wood-sorrel. At first, however, it was called the acid of sugar, or the saccharine acid.

As the earliest and best account of the oxalic acid was published by Bergman, he was for a long time reckoned the discoverer of it; but Mr Ehrhart, one of Scheele's intimate friends, informs us, that the world is indebted for its knowledge of this acid to that illustrious chemist \*, and Hermbstadt and Westrumb assign the discovery to the same author +. The assertions of these gentlemen, who had the best opportunity of obtaining accurate information, are certainly sufficient to establish the fact, that Scheele was the real discoverer of oxalic some nitric acid, and evaporation with the hear ... bias

1. Bergman gives us the following process for ob- Prepara. taining this acid : "Put one ounce of white sugar powdered into a tubulated retort, with three ounces of strong nitric acid, the specific gravity of which is to that of water as 1.567. When the solution is over, during which many fumes of the nitrous acid escape, let a receiver be fitted, and the liquor made to boil, by which abundance of nitrous gas is expelled. When the liquor in the retort acquires a reddish.brown colour. add three ounces more of nitric acid, and continue the

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<sup>\*</sup> Elwert's Magazine for Apothecaries, 1785, part i. p. 54. + Keir's Dictionary.

Book II. Divisiou II. boiling till the fumes cease, and the colour of the liquor vanishes. Then let the contents of the retort be emptied into a wide vessel; and, upon cooling, a crystallization will take place of slender quadrilateral prisms, which are often affixed to each other at an angle of 45°. These crystals, collected and dried on blotting paper, will be found to weigh 11 dr. 19 gr. By boiling the remaining lixivium with two ounces of nitric acid in the retort till the red fumes almost disappear, and by repeating the crystallization as before, 1/2 dr. 13 gr. of solid acid will be obtained. If the process be repeated once more upon the residuum, which has now a glutinous consistence, with the successive additions of small quantities of nitric acid, amounting in all to two ounces, a saline brown deliquescent mass will be formed, weighing half a dram, of which about a half will be lost by a farther purification. The crystals obtained thus at different times may be purified by solution and crystallization, and by digesting the last lixivium with some nitric acid, and evaporation with the heat of the 1. Bergman gives us the following process fee, nus

By the same process Bergman obtained it from gum arabic, alcohol, and honey : Scheele, Hermbstadt, Westrumb, Hoffman, &c. from a great variety of other vegetable productions; and Berthollet from a great number of animal substances.

It is of great consequence not to use too much nitric acid, otherwise the quantity of oxalic acid will be diminished; and if a very great quantity of nitric acid be used, no oxalic acid will be obtained at all \*. On the

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#### OXALIC: Janos

contrary, Hermbstadt affirms, that if too small a quantity of nitric acid be used, the acid obtained will not be the oxalic, but the tartaric. But I have not found this confirmed upon trying the experiment. A 100 grains of sugar, when properly treated, yield 58 grains of crystallized oxalic acid.

2. Oxalic acid, thus prepared, is in the form of four- Properties. sided prisms, whose sides are alternately larger, and they are terminated at the extremities by two-sided summits. They are transparent, and of a fine white colour, with considerable lustre : they have a very acid taste, and redden vegetable blues. These crystals contain a portion of water, as happens to most crystallized bodies. When cautiously heated on a sand-bath they fall to powder, and lose about a third of their weight; but a part of this loss is to be ascribed to acid volatilized. From an accurate set of experiments made on purpose to investigate this point, I conclude them to be composed of . 77 real acid

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So that the water of crystallization amounts very nearly to 4th of the weight \*.

3. When this crystallized acid is exposed to heat in Action of an open vessel, there arises a smoke from it, which affects disagreeably the nose and lungs. The residuum is a powder of a much whiter colour than the acid had been. By this process it loses 3 d of its weight, but soon recovers it again on exposure to the air. When dis-

• The reader is referred to a set of experiments by me on oxalic acid, published in the Phil. Trans. for 1807

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Book II. Division II. tilled, it first loses its water of crystallization, then liquefies and becomes brown; a little phlegm passes over, a white saline crust sublimes, some of which passes into the receiver; but the greatest part of the acid is destroyed, leaving in the retort a mass toth of the whole, which has an empyreumatic smell, blackens sulphuric acid, renders nitric acid yellow, and dissolves in muriatic acid without alteration. That part of the acid which sublimes is unaltered. When this acid is distilled a second time, it gives out a white smoke, which, condensing in the receiver, produces a colourless uncrystallizable acid, and a dark coloured matter remains behind \*. During all this distillation a vast quantity of elastic vapour makes its escape. From 279 grains of oxalic acid, Bergman obtained 109 cubic inches of gas, half of which was carbonic acid, and half carbureted hydrogen. Fontana from an ounce of it obtained 430 cubic inches of gas, one-third of which was carbonic acid, the rest carbureted hydrogen.

Of water.

4. The crystals of oxalic acid are soluble in their own weight of boiling water: water at the temperature of  $65.7^{\circ}$  dissolves half its weight of them. The specific gravity of the solution is 1.0593 †. One hundred parts of boiling alcohol dissolve 56 parts of these crystals; but at a mean temperature only 40 parts ‡. Liquid oxalic acid has a very acrid taste when it is concentrated, but a very agreeable acid taste when sufficiently diluted with water §.

It changes all vegetable blues except indigo to a red. One grain of crystallized acid, dissolved in 1920 grains

\* Bergman.

† Ibid, i. 255.

t Ibid. § Ibid.

of water, reddens the blue paper with which sugar loaves are wrapt: one grain of it, dissolved in 3600 grains of water, reddens paper stained with turnsol \*. According to Morveau, one part of the crystallized acid is sufficient to communicate a sensible acidity to 2633 parts of water t.

Its fixity is such, that none of it is sublimed when water containing it in solution is raised to the boiling temperature.

5. Oxalic acid is not affected by exposure to the air, Of simple bodies. or to the action of oxygen gas. The effect of the simple combustibles on it has not been tried; but in all probability is inconsiderable.

It is capable of oxidizing lead, copper, iron, tin, bismuth, nickel, cobalt, zinc, manganese.

It does not act upon gold, silver, platinum, mercury.

6. Oxalic acid combines with alkalies, earths, and metallic oxides, and forms salts known by the name of oxalates.

7. Muriatic and acetic acids dissolve oxalic acid, but without altering it 1. Sulphuric acid partly decomposes it by the assistance of heat, and a quantity of charcoal is formed. Nitric acid decomposes it at a boiling heat, and converts it into water and carbonic acid §. From this result, and from the products obtained by distilling pure oxalic acid, it follows, that this acid is composed of oxygen, hydrogen, and carbon. The best method of ascertaining the proportion of these constituents, is to distilat a red heat determinate quantities

\* Bergman, i. 255. t Bergman.

† Encyc. Method. art. Acids Saccharin. § Fourcroy, vii. 224.

Book II. Division II. of dry oxalates. So far as my experiments have gone, the oxalic acid is decomposed precisely in the same way, and the same new products formed whatever oxalate we use ; but the oxalate of lime is most convenient, because we can ascertain its composition with the great-When oxalate of lime is distilled in a est accuracy. small retort by means of a heat gradually raised to redness, the oxalic acid is completely decomposed and converted into five new substances; namely, water, carbonic acid, carbonic oxide, carbureted bydrogen, and charcoal. The water is small in quantity, the carbonic acid large, and partly in the state of gas, partly combined with the base of the oxalate. The carbonic oxide and carbureted hydrogen are in the state of gases, and in the proportion of about 21 of the former to 1 of the latter. The charcoal is small in quantity, and mixed with the residue in the retort, to which it gives a grey colour. By carefully ascertaining the proportion of each of these products, and estimating their composition according to the most exact analysis hitherto made of each, I found that the composition of oxalic acid may be stated as follows, oxygen 64

Composition.

oxygen 64 carbon 32 hydrogen 4

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This result differs very considerably from that announced by Fourcroy and Vauquelin as obtained by their experiments. Oxalic acid, according to them, is composed of oxygen 77, carbon 13, hydrogen 10\*. But I

\* Fourcroy, vii. 224.

#### OXALIC.

am persuaded that my numbers are much nearer the Chap. II. truth than these. The proportion of carbon contained in the carbonic acid, evolved by the distillation of oxalate of lime, is a good deal greater than the whole of the carbon which they assign to the composition of oxalic acid. A mister w Powerstood a planet and ath

This acid is too expensive to be employed for the purposes of domestic economy ; but it is extremely useful in chemistry to detect the presence of lime held in solution. For this purpose, either a little of the pure acid, or of the solution of oxalate of ammonia, is dropt into the liquid supposed to contain lime. If any be present, a white powder immediately precipitates \*. The reason of this is, that oxalate of lime is altogether insoluble, and oxalic acid in consequence is capable of taking lime from every other acid.

## · SECT. VIII.

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tion of these conternen, it is ountain

#### OF MELLITIC ACID.

THERE is a mineral of a honey-yellow colour which History. is found in small solitary crystals among the layers of Woodcoal at Arten in Thuringia. At first sight it has some resemblance to amber; but Werner recognised it

\* Provided the liquid does not contain an excess of any of the more powerful acids. In that case the excess must be saturated with ammonia before adding the oxalic acid.

Book II. Division II. as a peculiar substance about the year 1790, and gave it the name of *bonigstein* (honey-stone), which foreign mineralogists converted into *mellite*. This mineral is very rare. Hitherto indeed it has been found only in Thuringia and in Switzerland \*.

Mellite has usually a honey-yellow colour, but sometimes a straw-yellow. It is always crystallized in octahedrons, but they are rarely entire; sometimes indeed almost the whole of one of the pyramids is wanting. Their surface is generally smooth and brilliant, and interiorly they have a glassy lustre. They are semitransparent, brittle, soft, and easily reduced to powder. When pounded, they assume a yellowish-grey colour. Their specific gravity is about 1.550 <sup>+</sup>.

Mineralogists soon discovered that mellite is partly combustible; but they did not agree about its component parts. Lampadius and Abich undertook its chemical analysis about the same time. According to the first of these gentlemen, it is composed of

> 86·4 charcoal 3·5 bitumen 2·0 silica 3·0 water

#### 94.91

According to Abich, it contains the following ingredients

- \* Brochant's Mineralogy, ii. 75
- + Klaproth's Beitrage, iii. 115.
- t Crell's Annals, 1797, ii. 10.

#### MELLITIC.

40 carbonic acid

28 water

50 mm -

16 carbonate of alumina

5<sup>‡</sup> benzoic acid

5 benzoate of alumina

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- 3 oxide of iron
- 2<sup>t</sup> resin

#### 100 +

The results of these analyses differed so much from each other, that little confidence could be placed in either. Besides, it was evident from the way in which their experiments were conducted, that the original component parts of mellite had been altered by fire. Klaproth analysed it in 1799, and ascertained it to be a compound of alumina and a peculiar acid, to which he gave the name of mellitic 1. And this analysis was soon after confirmed by Mr Vauquelin ||.

1. Hitherto mellitic acid has been found only in the Preparamellite. It may be procured from that mineral by the following process : Reduce the mellite to powder, and boil it in about 72 times its weight of water. The acid combines with the water, and the alumina separates in flakes. By filtering the solution, and evaporating sufficiently, the mellitic acid is obtained in the state of crystals.

2. These crystals are either very fine needles, some- Properties. times collected into globules, or small short prisms.

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Ann. de Chim. XXXVI. 203.

tion.

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They have a brownish colour, and a taste at first sweetish-sour, and afterwards bitterish.

3. This acid is not very soluble in water; but the precise degree of solubility has not been ascertained.

4. When exposed to heat, it is readily decomposed, exhaling an abundant smoke, which however is destitute of smell. A small quantity of insipid ashes remain behind, which do not alter the colour of litmus paper.

5. All attempts to convert it into oxalic acid by the action of nitric acid have failed. The nitric acid merely caused it to assume a straw-yellow colour.

6. The effect of the simple bodies on this acid has not been tried.

7. It combines with alkalies, earths, and metallic oxides, and forms with them salts which are distinguished by the name of *mellates*. The properties of these compounds will be considered afterwards.

S. From the analysis of Mr Klaproth, we learn that the mellite is composed of

46 mellitic acid 16 alumina 38 water

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## mentive the mellitic acto is 001 and an the

Now when mellite is distilled in a retort, the acid is completely decomposed, and its elements combine together in a different way. By this method Mr Klaproth obtained from 100 grains of mellite

54 cubic inches of carbonic acid gas

13 ..... hydrogen gas
38 grains of acidulous and aromatic water
1..... aromatic oil

### 9 ..... charcoal 16.....alumina

From this analysis it is obvious, that mellitic acid is composed of carbon, hydrogen, and oxygen, like most of the combustible acids. It does not, however, furnish us with sufficient data for ascertaining the proportion of these constituent parts.

Mellitic acid bears a great resemblance to the oxalic; but it differs from it in many particulars, especially in the nature of the compounds which it forms with different bases.

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# SECT. IX.

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TARTAR, OF CREAM OF TARTAR, as it is commonly History. called when pure, has occupied the attention of chemists for several centuries. Duhamel and Grosse, and after them Margraff and Rouelle the Younger, proved that it was composed of an acid united to potash; but Scheele was the first who obtained this acid in a separate state. He communicated his process for obtaining it to Retzius, who published it in the Stockholm Transactions for 1770. It consisted in boiling tartar with chalk, and in decomposing the tartrate of lime thus formed by means of sulphuric acid.

1. The process employed at present for obtaining tar- Preparataric acid, which is the same with that of Scheele, is the following : Dissolve tartar in boiling water, and add

tion.

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Book II. Division II. to the solution powdered chalk till all effervescence ceases, and the liquid does not redden vegetable blues. Let the liquid cool, and then pass it through a filter. A quantity of tartrate of lime (which is an insoluble white powder) remains upon the filter. Put this tartrate, previously well washed, into a glass cucurbite, and pour on it a quantity of sulphuric acid equal to the weight of the chalk employed, which must be diluted with water. Allow it to digest for 12 hours, stirring it occasionally. The sulphuric acid displaces the tartaric : sulphate of lime remains at the bottom, while the tartaric acid is dissolved in the liquid part. Decant off this last, and try whether it contains any sulphuric acid. This is done by dropping in a little acetate of lead; a precipitate appears, which is insoluble in acetic acid if sulphuric acid be present, but soluble if it be absent. If sulphuric acid be present, the liquid must be digested again on some more tartrate of lime ; if not, it is to be slowly evaporated, and about one third part of the weight of the tartar employed is obtained of crystallized tartaric acid.

Lime may be substituted for chalk in this process. In that case the decomposition of the tartar is complete; whereas by Scheele's method, the excess of acid only combines with the chalk; but when lime is used, the whole tartrate of lime by no means separates. A considerable portion is retained in solution by the potash of the tartar now disengaged. If the liquid be evaporated, this portion appears under the form of a transparent jelly. By exposure to the air the potash attracts carbonic acid, which unites to the lime, while the tartaric acid combines again with the potash. To obtain the potash in a state of tolerable purity, the best me-

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#### TARTARIC.

thod, according to Vauquelin, to whom we are indebted for these observations, is to evaporate to dryness, and heat the residue to redness. By lixiviating the mass, the potash will be obtained in a state of considerable purity \*.

2. The form of the crystals of tartaric acid is so ir- Properties. regular, that every chemist who has treated of this subject has given a different description of them. According to Bergman, they generally consist of divaricating lamellæ +; according to Van Packen, they assume oftenest the form of long-pointed prisms 1; Spielman and Corvinus § obtained them in groups, some of them lance-shaped, others needle-formed, others pyramidal. Morveau obtained them needle-form ||. Their specific gravity is 1.5962 ¶.

As they are sold by apothecaries in this country, they are in groups, and appear to be very irregular four-sided. prisms. By my experiments they are composed of \$4.5 real acid and 15.5 of water.

3. Crystallized tartaric acid is white, and very firm, and is but imperfectly transparent. It may be exposed to the air for any length of time without undergoing any change. When heated a few degrees above 212° it melts and remains limpid and transparent like water. At 250° it boils without losing its transparency or becoming coloured. If the boiling be continued for a short time only it does not lose above 4 per cent. of its

\* Ann. de Chim. xlvii. 147. ‡ De Sale Essent. Acidi Tartari. || Encyc. Method. Chim. i. 323. " Hassenfratz, Ann. de Chim. xxxviii. II.

+ Bergman, iii. 368. Analecta de Tartaro.

Book II. Division II. weight. On cooling it concretes again into a hard semitransparent mass, very much resembling a quantity of white sugar that has been melted at the same temperature. By this process the nature of the acid is changed. It now deliquesces when exposed to the air.

In the open fire tartaric acid burns without leaving any other residuum than a spongy charcoal, which generally contains a little lime. When distilled in close vessels, it is converted into carbonic acid gas and carbureted hydrogen gas, a coloured oil, and a reddish acid liquor, which was formerly distinguished by the name of *pyrotartarous acid*, but which Fourcroy and Vauquelin have lately ascertained to be merely acetic acid impregnated with oil \*.

When tartaric acid combined with a base, as with lime, is distilled in a sufficiently strong heat, it is completely decomposed. The products into which it is converted, are, water, carbonic acid, beavy inflammable air, oil and charcoal. The quantity of carbonic acid which it yields is less than what is furnished by an equal weight of oxalic acid; but it differs from oxalic acid, in yielding a portion of brown coloured thick oil, which has an empyreumatic smell, and dissolves in alcohol.

4. Tartaric acid dissolves readily in water. Bergman obtained a solution, the specific gravity of which was 1.230<sup>†</sup>. Morveau observed, however, that crystals formed spontaneously in a solution, the specific gravity of which was 1.084. It is not liable to spon-

\* Ann. de Chim. XXXV. 131.

+ Bergman, i. 250.

#### TARTARIC. 100

taneous decomposition when dissolved in water, unless the solution be considerably diluted.

5. Neither its action on oxygen gas nor on simple combustibles and incombustibles has been examined; Action of but it is probable that it is not capable of producing any dies. sensible change on them. It is capable of oxidizing iron and zinc, and even mercury; but it does not act upon antimony, bismuth, tin, lead, copper, silver, gold, nor platinum. Its action on the other metallic bodies has scarcely been examined.

. 6. It combines with alkalies, earths, and metallic oxides, and forms salts known by the name of tartrates. Though it forms with the alkaline earths salts which are scarcely soluble in water, yet it has not the property of precipitating any of them from their solutions. In this respect it differs very greatly from oxalic acid, which precipitates them all except magnesia.

7. The action of the greater part of the other acids on it is unknown. Hermbstadt has ascertained, that it may be converted into oxalic acid by distilling it repeatedly with six times its weight of nitric acid. By this process he obtained 560 parts of oxalic acid from 360 parts of tartaric acid 1.

8. From this result, and from the products obtained when tartaric acid is distilled, it is evident that it is Composicomposed of oxygen, carbon, and hydrogen. Fourcroy informs us, that Vauquelin and he have ascertained that these ingredients are combined in it in the following proportions \*:

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Chap. 11.

t Crell's N. End. in d. Chem. 1782. p. 76. # Fourcroy, vii: 261.

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Book II. Division II. 70.5 oxygen 19.0 carbon 10.5 hydrogen

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Tartaric acid, in a state of purity, has scarcely been put to any use; but some of the compounds into which it enters are much employed in medicine. This acid has the property of combining in two different proportions with a great number of bases. With potash, for instance, in one proportion, it forms a salt pretty soluble in water, called *tartrate of potasb*; but when added in a greater proportion, it forms *tartar*, a salt very imperfectly soluble in water. By this property, the presence of tartaric acid in any acid solution may easily be detected. All that is necessary is to drop in slowly a little solution of potash: if tartaric acid be present, tartar immediately precipitates in the form of a white gritty powder.

## SECT. X.

#### OF CITRIC ACID.

History.

CHEMISTS have always considered the juice of oranges and lemons as an acid. This juice contains a quantity of mucilage and water, which renders the acid impure, and subject to spontaneous decomposition. Mr Georgius took the following method to separate the mucilage. He filled a bottle entirely with lemon-juice, cork-

ed it, and placed it in a cellar : in four years the liquid was become as limpid as water, a quantity of mucilage had fallen to the bottom in the form of flakes, and a thick crust had formed under the cork. He exposed this acid to a cold of 23°, which froze a great part of the water, and left behind a strong and pretty pure acid \*. It was Scheele, however, that first pointed out a method of obtaining this acid perfectly pure, and who demonstrated that it possesses peculiar properties.

1. His process, which is still followed, is this : Satu- Preparation rate lemon juice, while boiling, with powdered chalk. A white powder falls to the bottom, which is lime combined with citric acid. Separate this powder, and wash it with warm water till the water passes off colourless. Then pour upon it as much sulphuric acid as will saturate the chalk employed, having previously diluted it with six times its weight of water. Boil the mixture for some minutes, and pass it through a filter to separate the sulphate of lime. The liquid is then to be evaporated to the consistence of a syrup, and set aside to cool. A number of crystals form in it : these are citric acid t.

Mr Scheele advises the use of an excess of sulphuric acid in order to ensure the separation of all the lime: but according to Dizé, this excess is necessary for another purpose t. A quantity of mucilage still adheres to the citric acid in its combination with lime, and sulphuric acid is necessary to decompose this mucilage; which, as Fourcroy and Vauquelin have proved, it is

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\* Stockbolm Transactions; 1774. † Nicholson's Journal, ii. 43. Vol. II.

+ Scheele, ii. 203.

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tion.

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capable of doing. His proof of the presence of mucilage is, that when the solution of citric acid in water, which he had obtained, was sufficiently concentrated by evaporation, it assumed a brown colour, and even became black towards the end of the evaporation. The crystals also were black. By repeated solutions and evaporations, this black matter was separated, and found to be charcoal. Hence he concluded that mucilage had been present; for mucilage is composed of carbon, hydrogen, and oxygen; sulphuric acid causes the hydrogen and oxygen to combine and form water, and charcoal remains behind. It is not certain, however, as Mr Nicholson remarks very justly \*, that the sulphuric acid may not act upon the citric acid itself, and that the charcoal may not proceed from the decomposition of it; at least the experiments of Mr Dizé are insufficient to prove the contrary. In that case, the smaller the excess of sulphuric acid used the better.

Proust, who has published a memoir on the preparation of citric acid in the *Journal de Physique* for 1801 +, has observed that this is actually the case. When too much sulphuric acid is employed, it acts upon the citric acid, chars it, and prevents it from crystallizing. This error is remedied by adding a little chalk. This chemist has ascertained, that four parts of chalk require for saturation 94 parts of lemon juice. The citrate of lime obtained amounts to  $7\frac{1}{2}$  parts. To decompose this, 20 parts of sulphuric acid, of the specific gravity 1.15, are necessary.

Properties.

2. The crystals of citric acid are rhomboidal prisms,

\* Nicholson's Journal, ii. 43.

+ Jour. de Phys. lii. 366.

#### CITRIC.

the sides of which are inclined to each other at angles of about 120 and 60 degrees, terminated at each end by four trapezoidal faces, which include the solid angles \*. They are not altered by exposure to the air. Their taste is exceedingly acid, and even excites pain; but when the acid is properly diluted with water, the acidity is pleasant.

3. When exposed to the open fire, it first melts, then swells up and exhales an acrid vapour, and leaves behind it a small quantity of charcoal. When distilled in close vessels, it partly evaporates without decomposition, and is partly converted into acetic acid, carbonic acid, and carbureted hydrogen gas, which pass over, and charcoal which remains in the retort.

4. Citric acid is exceedingly soluble in water. According to Vauquelin, 100 parts of it require only 75 parts of water. Boiling water dissolves twice its weight of it †. This solution may be kept a long time in close vessels; however it at last putrifies, and is decomposed.

5. Neither oxygen gas nor the simple combustibles or incombustibles produce any effect upon it. It is capable of oxidizing iron, zinc, tin. It does not act upon gold, silver, platinum, mercury, bismuth, antimony, arsenic.

6. It combines with alkalies, earths, and metallic oxides, and forms salts known by the name of *citrates*.

7. The action of none of the acids on it has been examined, if we except that of the sulphuric and nitric. Sulphuric acid, when concentrated, converts it into a-

Action of acids ]

\* Dizé, Nicholson's Journal, ii. 33. † Dizé.

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cetic acid \*. Scheele said that he could not convert it into oxalic acid by means of nitric acid, as he had done several other acids : but Westrumb affirms, that this conversion may be affected; and thinks that Scheele had probably failed from having used too large a quantity of nitric acid, by which he had proceeded beyond the conversion into oxalic acid, and had changed the citric acid into vinegar : and in support of his opinion, he quotes his own experiments; from which it appeared that, by treating 60 grains of citric acid with different quantities of nitric acid, his products were very different. Thus with 200 grains of nitric acid he got 30 grains of oxalic acid; with 300 grains of nitric acid he obtained only 15 grains of the oxalic acid; and with 600 grains of nitric acid no vestige appeared of the oxalic acid. On distilling the products of these experiments, especially of the last, he obtained vinegar mixed with nitric acid. The experiments of Westrumb have been confirmed by Fourcroy and Vauquelin; who, by treating citric acid with a great quantity of nitric acid, converted it into oxalic and acetic acids. The proportion of the first was much smaller than that of the second.

From these experiments it is evident that its component parts are oxygen, hydrogen, and carbon; but the proportions of them have not been ascertained.

The use of this acid as a seasoner of food, and in preparing an agreeable cooling drink called *lemonade*, is well known.

# Fourcroy, vii. 206.

#### KINIC.

### SECT. XI.

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#### OF KINIC ACID.

MR DESCHAMPS, junior, an apothecary in Lyons, some Discovery. time ago published a method of extracting from yellow Peruvian bark a peculiar salt, to which the physicians of Lyons ascribed the febrifuge properties of that bark. His process was very simple ; the bark was macerated in cold water, and the infusion concentrated by evaporation. It was then set aside for some time in an open vessel. The crystals of the salt gradually formed and separated, and they were purified by repeated crystallizations. From 100 parts of the bark about 7 parts of these crystals were obtained \*.

This salt has been lately examined by Mr Vauquelin, who has proved that it is composed of lime united to a peculiar acid hitherto unknown. To this acid he has given the name of kinic, borrowed from the term quinquina, applied by the French writers to the bark from which the salt was extracted. 1115 004

Deschamp's salt then is kinate of lime. It possesses Kinate of durantie lime. the following properties.

Its colour is white, it crystallizes in square or rhomboidal plates; it has no taste, and is flexible under the teeth. It dissolves in about five times its weight of

\* Ann. de Chim. xlviii. 162. of raise called Association of The attention and carefy in

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water at the temperature of 55°. It is insoluble in alcohol.

When placed on burning coals it swells, gives out a smell like tartar, and leaves a mixture of carbonate of lime and charcoal. The fixed alkalies and their carbonates precipitate lime from the solution of this salt, but ammonia produces no effect. Sulphuric and oxalic acid precipitate lime likewise, but no precipitate is produced by acetate of lead or nitrate of silver. The infusion of tannin occasions a flaky yellow precipitate.

Separation of kinic acid. Mr Vauquelin separated the lime from the kinic acid by means of oxalic acid. The oxalate of lime obtained from 100 grains of the salt weighed 27 grains. Hence he concluded that the salt was a compound of \$5 parts acid and 15 lime. But the lime in 27 grains of oxalate of lime very little exceeds 10 grains. Hence the salt ought to be composed of 90 parts acid and 10 of lime.

Properties.

The kinic acid, thus freed from lime, was concentrated by evaporation to the consistency of a syrup, and then set aside for a week. No crystals formed in it spontaneously; but upon being touched with a glass rod it wholly crystallized at once in divergent plates.

Its colour was slightly brown (doubtless from some impurity); its taste was extremely acid and somewhat bitter, probably because it was not quite free from the other constituents of the bark. It was not altered by being left exposed to the air.

On burning coals it melted, froathed, blackened, and exhaled in acrid vapours, leaving only a little charcoal behind.

It combines with the different bases, and forms a set of salts called *kinates*. The alkaline and earthy ki-

#### SACLACTIC.

nates are soluble and crystallizable. This ac does Chap. II. not precipitate nitrates of silver, mercury, nor lead \*.

This detail, though imperfect, is sufficient to distinguish the kinic from every other acid. Its decomposition by heat shows that it belongs to the class of combustible acids. Its crystallizing, its great solubility in water, and its forming a soluble salt with lime, and not precipitating silver nor lead, sufficiently distinguish it from all the other combustible acids with which it might be confounded.

## SECT. XII.

## OF SACLACTIC ACID.

South making .

THIS acid was discovered by Scheele in 1780. After History. having obtained oxalic acid from sugar, he wished to examine whether the sugar of milk would furnish the same product. Upon four ounces of pure sugar of milk, finely powdered, he poured 12 ounces of diluted nitric acid, and put the mixture in a large glass retort, which he placed in a sand-bath. A violent effervesence ensuing, he was obliged to remove the retort from the sand-bath till the commotion ceased. He then continued the distillation till the mixture became yellow. As no crystals appeared in the liquor remaining in the retort after standing two days, he repeated the distilla-

\* Ann. de Chim. lix. 162.

Book H. Division II. tion as before, with the addition of eight ounces of nitric acid, and continued the operation till the yellow colour, which had disappeared on the addition of the nitric acid, returned. The liquor in the retort contained a white powder, and when cold was observed to be thick. Eight ounces of water were added to dilute this liquor, which was then filtrated, by which the white powder was separated; which being edulcorated and dried, weighed 71 dr. The filtrated solution was evaporated to the consistence of a syrup, and again subjected to distillation, with four ounces of nitric acid as before; after which, the liquor, when cold, was observed to contain many small, oblong, sour crystals, together with some white powder. This powder being separated, the liquor was again distilled with more nitric acid as before; by which means the liquor was rendered capable of yielding crystals again ; and by one distillation more, with more nitric acid, the whole of the liquor was converted into crystals. These crystals, added together, weighed five drams; and were found, upon trial, to have the properties of the oxalic acid.

Mr Scheele next examined the properties of the white powder, and found it to be an acid of a peculiar nature; he therefore called it the *acid of the sugar of* milk\*. It was afterwards called *saclactic* acid by the French chemists. Fourcroy has lately given it the name of mucous acid, because it is obtained by treating gum arabic, and other mucilaginous substances, with nitric acid.

\* Scheele, ii. 69.

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Mr Hermbstadt of Berlin had made similar experi-Chap. II. ments on sugar of milk at the same time with Scheele. and with similar results; but he concluded that the white powder which he obtained was nothing else than oxalate of lime with excess of acid, as indeed Scheele himself did at first. After he became acquainted with Scheele's conclusions, he published a paper in defence of his own opinion; but his proofs are very far from establishing it, or even rendering its truth probable \*. He acknowledges himself, that he has not been able to decompose this supposed salt; he allows that it possesses properties distinct from the oxalic acid; but he ascribes this difference to the lime which it contains : yet all the lime which he could discover in 240 grains of this salt was only 20 grains; and if the alkali which he employed was a carbonate (as it probably was), these 20 must be reduced to 11. Now Morveau has shown, that oxalic acid, containing the same quantity of lime, exhibits very different properties. Besides, this acid, whatever it is, when united with lime, is separated by the oxalic, and must therefore be different from it. as it would be absurd to suppose that an acid could displace itself+. The saclactic acid must therefore be considered as a distinct acid, since it possesses peculiar properties,

1. Saclactic acid may be obtained by the following Preparaprocess : Upon one part of gum arabic, or other similar gum, previously put into a retort, pour two parts of nitric acid. Apply a slight heat for a short time, till a

tion.

\* Crell's Annals, 1784, ii. 509. + Moryeau, Encyc. Method, i. 291.

Book II. Division IJ. little nitrous gas and carbonic acid gas comes over; then allow the mixture to cool. A white powder gradually precipitates, which may be easily separated by filtration. This powder is saclactic acid \*.

Properties.

2. Saclactic acid, thus obtained, is under the form of a white gritty powder, with a slightly acid taste.

Heat decomposes it. When distilled, there comes over an acid liquor which crystallizes in needless on cooling, a red coloured acrid oil, carbonic acid gas, and carbureted hydrogen gas. There remains in the retort a large proportion of charcoal.

Saclactic acid, according to Scheele, is soluble in 60 parts of its weight of boiling water; but Messrs Hermbstadt  $\ddagger$  and  $\ddagger$  Morveau found, that boiling water only dissolved  $\frac{1}{80}$ th part: it deposited about  $\frac{1}{4}$ th part on cooling in the form of crystals §.

The solution has an acid taste, and reddens the infusion of turnsol ||. Its specific gravity, at the temperature of  $53 \cdot 7^{\circ}$ , is 1.0015 ¶.

The compounds which it forms with earths, alkalies, and metallic oxides, are denominated *saccolates*. These salts are but very imperfectly known, no chemist having examined them except Scheele. The facts which he ascertained are the following:

With potash it forms a salt soluble in eight parts of boiling water, which crystallizes on cooling. The saccolate of soda also crystallizes, and is soluble in five parts of water. Saccolate of ammonia loses its base by

- \* Fourcroy, vii. 146. † Encyc. Method. i. 290.
- FId.

+ Pbys. Chem. § Scheele. ¶ Morveau, Ibid. a moderate heat, while the acid remains behind. The compounds which it forms with the earths are nearly insoluble in water. It scarcely acts upon any of the metals, but it combines with their oxides : it forms salts almost insoluble in water. When poured into the nitrates of silver, mercury, or lead, it occasions a white precipitate. It produces no change in the sulphates of iron, copper, zinc, manganese, nor in the muriates of tin and mercury \*.

## SECT. XIII.

tor, in which he comprises his it

## OF URIC ACID.

**V**ARIOUS attempts were made by chemists to ascertain the nature of the calculous concretions which occasionly form in the kidneys and bladder, and produce one of the most painful diseases to which we are liable. These attempts were attended with very little success, till Scheele published a set of experiments on the subject in 1776. He examined several of these urinary calculi, and found them composed chiefly of a peculiar acid, the properties of which he described. His resul were soon after confirmed by Bergman, who had engaged in a similar set of experiments about the same time  $\dagger$ . To the acid thus discovered, Morveau gave a first the name of *bezoardic*, which was after changed i

\* Scheele, ii. 76. † Ibid. i. 199 and 210. French Trans.

Discovery.

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Book II. Division II. to *lithic* by the French chemists, when they contrived the new chemical nomenclature in 1787. This last term, in consequence chiefly of the observations and objections of Dr Pearson, has been recently laid aside, and the name *uric acid* substituted in its place.

Scheele ascertained that uric acid exists always in human urine. Experiments on the urinary calculi were published by Mr Higgins in 1789 \*, and by Dr Austin in 1791; but little was added to our knowledge of uric acid till Dr Wollaston published his admirable paper on the calculous concretions in 1797. Dr Pearson published a copious set of experiments on the same subject in 1798, in which he enumerates his trials on uric acid, and endeavours to prove that it is not entitled to the name of acid, but ought to be classed among animal oxides. This drew the attention of Fourcroy and Vauquelin to the subject : they published an excellent treatise on urinary calculi, in which they demonstrate that it possesses the properties of an acid, and confirm the observations of Bergman and Scheele. But for the most complete account of uric acid we are endebted to Dr William Henry, who made it the subject of his thesis published in 1807.

Preparation. 1. To obtain pure uric acid, Dr Henrydissolved pulverized calculi (previously known to be composed chiefly of that acid) in a ley of potash, and precipitated the uric acid by means of muriatic or acetic acids. The powder thus obtained was first washed with a little ammonia, to remove any adhering foreign acid, and

\* Comparative view of the phlogistic and antiphlogistic theories, p. 283.

then edulcorated with a sufficient quantity of warm Chap. II. water.

2. Uric acid thus obtained is a white powder, which properties. feels harsh but not gritty, and is destitute both of taste and smell. It reddens the infusion of litmus. It dissolves in 1720 parts of water at the temperature of 60°. and in 1150 parts of boiling water. As this last solution cools, it deposites minute crystals of uric acid. The watery solution reddens litmus, but produces no precipitate when dropt into earthy or metallic salts \*.

3. It is rapidly dissolved by fixed alkaline solutions, but less readily by ammonia. The alkaline carbonates have no effect on it whatever t.

4. It decomposes the alkaline hydrosulphurets, and precipitates their sulphur. It likewise decomposes soap, provided a sufficient quantity of it be employed t.

5. It dissolves in nitric acid; and when the solution is evaporated nearly to dryness, it assumes a fine pink colour, which becomes much deeper when water is added, so as to have a near resemblance to carmine. In this state it stains wood, the skin, &c. of a beautiful red colour. The watery solution of this matter loses its red colour in a few hours, and it cannot afterwards be restored §.

When the solution of uric in nitric acid is boiled, a quantity of azotic gas, carbonic acid gas, and of prussic acid, is disengaged ||. Dr Pearson, by repeated distillations, converted the residue into nitrate of ammonia. When oxymuriatic acid gas is made to pass into water

# Henry. + Scheele, Fourcroy, and Henry. § Scheele, Bergman, Pearson, and Henry. t Henry. || Fourcroy, Ann. de Chim. XXVII. 267.

Book II. Division II. containing this acid suspended in it, the acid assumes a gelatinous appearance, then dissolves; carbonic acid gas is emitted, and the solution yields by evaporation muriate of ammonia, superoxalate of ammonia, muriatic acid, and malic acid \*.

6. It combines with the different bases, and forms a genus of salts called *urates*; for the examination of which we are chiefly indebted to Dr Henry.

7. When tric acid is distilled, about a fourth of the acid passes over altered in its properties, and is found in the receiver crystallized in plates; a few drops of thick oil make their appearance;  $\frac{1}{8}$ th of the acid of concrete carbonate of ammonia, some prussiate of ammonia, some water, and carbonic acid pass over; and there remains in the retort charcoal, amounting to about  $\frac{1}{8}$ th of the weight of the acid distilled  $\frac{1}{7}$ . According to Dr Henry, the decomposition goes on in the following manner: 1. A drop or two of water holding carbonate of ammonia in solution passes into the receiver; 2. Dry carbonate of ammonia; 3. The acid sublimate; 4. The coal in the retort amounts to about  $\frac{1}{6}$ th of the calculus distilled.

Sublimate from uric acid. The nature of the acid sublimate has been particularly examined by Dr William Henry. Scheele had considered it as analogous to succinic acid, and Dr Pearson as approaching to benzoic acid in its properties. According to Dr Henry, it is a salt composed of a *peculiar* acid combined with ammonia. The following he found to be its properties.

\* Brugnatelli, Ann. de Chim. xxvi'. 267. Fourcroy, x. 222.

+ Fourcroy, Ann. de Chim. xvi. 116.

Its colour is yellow, and it has a cooling bitter taste. It dissolves readily in water, and in alkaline solutions, from which it is not precipitated by acids. It dissolves also sparingly in alcohol. It is volatile; and when sublimed a second time, becomes much whiter. The watery solution reddens vegetable blues; but a very small addition of ammonia destroys this property. It does not produce an effervescence with alkaline carbonates. By evaporation it yields permanent crystals, but ill defined, from a portion of animal matter adhering. They redden vegetable blues. Potash, when added to these crystals, disengages ammonia. When dissolved in nitric acid they do not leave a red stain, as happens with uric acid ; nor does their solution in water decompose the earthy salts, as happens with the alkaline urates : neither has it any action on the salts of copper, iron, gold, platinum, tin, or mercury. With nitrates of silver and mercury, and acetate of lead, it forms a white precipitate soluble in an excess of nitric acid. Muriatic acid occasions no precipitate in the solution of these crystals in water. These properties show us, that the acid of the sublimate is different from the uric, and from every other known acid. Dr Austin found, that by repeated distillations it was resolved into ammonia, azote, and prussic acid. Hence its constituents are doubtless the same as those of uric acid, varying only in proportion.

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SECT. XIV.

### OF LACCIC ACID.

History.

About the year 1786, Dr Anderson of Madras mentioned, in a letter to the governor and council of that place, that nests of insects, resembling small cowry shells, had been brought to him from the woods by the natives, who eat them with avidity. These supposed nests he soon afterwards discovered to be the coverings of the females of an undescribed species of coccus, which he shortly found means to propagate with great facility on several of the trees and shrubs growing in his neighbourhood \*.

On examining this substance, which he called *white* lac, he observed in it a very considerable resemblance to bees wax; he noticed also, that the animal which secretes it provides itself by some means or other with a small quantity of honey, resembling that produced by our bees; and in one of his letters he complains, that the children whom he employed to gather it were tempted by its sweetness to eat so much of it as materially to reduce the product of his crop. Small quantities of this matter were sent into Europe in 1780, both in its

\* The Chinese collect a kind of wax, which they call *pe-la*, from a coccus, deposited for the purpose of breeding on several shrubs, and manage it exactly as the Mexicans manage the cochineal insect. It was the knowledge of this that induced Dr Anderson to attempt to propagate his insect.

#### LACCIC.

natural state and melted into cakes; and in 1793 Dr Chap. II. Pearson, at the request of Sir Joseph Banks, undertook a chemical examination of its qualities, and his experiments were published in the Philosophical Transactions for 1794.

A piece of white lac, from 3 to 15 grains in weight, is probably produced by each insect. These pieces are of a grey colour, opaque, rough, and roundish. When white lac was purified by being strained through muslin, it was of a brown colour, brittle, hard, and had a bitterish taste. It melted in alcohol, and in water of the temperature of 145°. In many of its properties it resembles bees wax, though it differs in others; and Dr Pearson supposes that both substances are composed of the same ingredients, but in different proportions.

1. Two thousand grains of white lac were exposed in Properties. such a degree of heat as was just sufficient to melt them. As they grew soft and fluid, there oozed out 550 grains of a reddish watery liquid, which smelled like newly baken bread \*. To this liquid Dr Pearson has given the name of of laccic acid +.

2. It possesses the following properties :

It turns paper stained with turnsol to a red colour.

After being filtered, it has a slightly saltish taste with bitterness, but is not at all sour.

When heated, it smells precisely like newly baken hot bread. The belos of the belos of the belos of the

aperatore, o blackish matter wo

\* The same liquid appears on pressing the crude lac between the fingers; and we are told that when newly gathered it is replete with juice.

+ Pearson's Transl. of the Chemical Nomenclature. Vol. II. Y

Book II. Division II.

On standing, it grows somewhat turbid, and deposits a small quantity of sediment.

Its specific gravity at the temperature of 60° is 

A little of it having being evaporated till it grew very turbid, afforded on standing small needle-shaped crystals in mucilaginous matter.

Two hundred and fifty grains of it were poured into a very small retort and distilled. As the liquor grew warm, mucilage.like clouds appeared ; but as the heat increased they disappeared again. At the temperature of 200° the liquor distilled over very fast ; a small quantity of extractive matter remained behind. The distilled liquor while hot smelled like newly baken bread, and was perfectly transparent and yellowish. A shred of paper stained with turnsol, which had been put into the receiver, was not reddened : nor did another which had been immersed in a solution of sulphate of iron, and also placed in the receiver, turn to a blue colour upon being moistened with the solution of potash \*.

About 100 grains of this distilled liquid being evaporated till it grew turbid, after being set by for a night, afforded acicular crystals, which under a lens appeared in a group not unlike the umbel of parsley. The whole of them did not amount to the quarter of a grain. They tasted only bitterish.

Another 100 grains being evaporated to dryness in a very low temperature, a blackish matter was left behind, which did not entirely disappear on heating the spoon containing it very hot in the naked fire; but on

\* A proof that the acid was not the pression

#### LACCIC.

heating oxalic acid to a much less degree, it evaporated, Chap. II. and left not a trace behind.

Carbonate of lime dissolved in this distilled liquid with effervescence. The solution tasted bitterish, did not turn paper stained with turnsol red, and on adding to it carbonate of potash a copious precipitation ensued. A little of this solution of lime and of alkali being evaporated to dryness, and the residuum made red hot, no= thing remained but carbonate of lime and carbonate of potash.

This diquid did not render nitrate of lime turbid, but it produced turbidness in nitrate and muriate of barytes.

To 500 grains of the reddish-coloured liquor obtained by melting white lac, carbonate of soda was added till the effervescence ceased, and the mixture was neutralized; for which purpose three grains of the carbonate were necessary. During this combination a quantity of mucilaginous matter, with a little carbonate of lime, was precipitated. The saturated solution being filtrated and evaporated to the due degree, afforded on standing deliquescent crystals, which on exposure to fire left only a residuum of carbonate of soda.

Lime-water being added to this reddish-coloured liquor, produced a light purple turbid appearance; and on standing there were clouds just perceptible.

Sulphuret of lime occasioned a white precipitation. but no sulphureted hydrogen gas was perceptible by the smell.

Tincture of galls produced a green precipitation,

Sulphate of iron produced a purplish colour, but no precipitation; nor was any precipitate formed by the addition first of a little vinegar, and then of a little potash to the mixture.

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Acetate of lead occasioned a reddish precipitation, which redissolved on adding a little nitric acid.

Nitrate of mercury produced a whitish turbid liquor.

Oxalic acid produced immediately the precipitation of white acicular crystals, owing probably to the presence of a little time in the liquid.

Tartrate of potash produced a precipitation not unlike what takes place on adding tartaric acid to tartrate of potash; but it did not dissolve again on adding potash.

Such were the properties of this acid discovered by Dr Pearson \*. Before this acid can be admitted as a peculiar substance, it would be necessary to subject it to a more rigid examination. The quantity which Dr Pearson examined was by far too small to enable him to obtain satisfactory results.

## SECT. XV.

#### OF MALIC ACID.

Prepara-

1. THIS acid, which was discovered by Scheele in 1785, has received the name of *malic acid*, because it may be obtained in abundance from the juice of apples, in which it exists ready formed. Scheele has given us the following process for extracting it: Saturate the juice of apples with potash, and add to the solution ace-

\* Phil. Trans. 1794, p. 382.

tate of lead till no more precipitation ensues. Wash Chap. II. the precipitate carefully with a sufficient quantity of water; then pour upon it diluted sulphuric acid till the mixture has a perfectly acid taste, without any of that sweetness which is perceptible as long as any lead remains dissolved in it; then separate the sulphate of lead, which has precipitated, by filtration, and there remains behind pure malic acid \*.

Vauquelin has lately ascertained that it may be extracted, with greater advantage, from the juice of the sempervivum tectorum, or common house-leek, where it exists abundantly combined with lime. The process which he found to answer best is the following: To the juice of the house-leek add acetate of lime as long as any precipitate takes place. Wash the precipitate, and decompose it by means of diluted sulphuric acid in the manner directed by Scheele t.

Malic acid may be formed also by the action of nitric acid on sugar. If nitric acid be distilled with an equal quantity of sugar, till the mixture assumes a brown colour (which is a sign that all the nitric acid has been extracted from it), this substance will be found of an acid taste; and after all the oxalic acid which may have been formed is separated by lime-water, there remains another acid, which may be obtained by the following process : Saturate it with lime, and filter the solution; then pour upon it a quantity of alcohol, and a coagulation takes place. This coagulum is the acid combined with lime. Separate it by filtration, and edul-

> \* Swedish Trans. and Crell's Annals for 1785. Ann. de Chim. XXXIV. 127.

Book II. Div sion II. corate it with fresh alcohol; then dissolve it in distilled water, and pour in acetate of lead till no more precipitation ensues. The precipitate is the acid combined with lead, from which it may be separated by diluted sulphuric acid \*.

Bouillon La Grange has lately endeavoured to prove, that this acid is nothing else than the acetic combined with a peculiar vegetable matter. He has shown that acetic acid exists in the juice of apples, and thinks he has proved that nitric acid forms with sugar a peculiar extractive stuff which exists also in apples †. But his observations do not appear to me to prove the coincidence between acetic and malic acids, as they possess properties so very different from each other.

Properties.

2. Malic acid, thus obtained, is a liquid of a reddish brown colour and a very acid taste, When evaporated it becomes thick and viscid like a mucilage or syrup, but it does not crystallize. When exposed to a dry atmosphere in thin layers, it dries altogether, and assumes the appearance of varnish.

When heated in the open fire it becomes black, swells up, exhales an acrid fume, and leaves behind it a very voluminous coal. When distilled, the products are an acid water, a little carbureted hydrogen gas, and a large proportion of carbonic acid ‡.

3. It is very soluble in water. It gradually decomposes spontaneously, by undergoing a kind of fermentation in the vessels in which it is kept.

4. Sulphuric acid chars it, and nitric acid converts it

\* Swedish Trans. and Crell's Annals for 1785.

† Gehlen's Jour. 2d Seres. ii. 173. ‡ Fourcroy, vii. 199.

#### MALIC.

into oxalic acid \*. Hence it is evident that it is composed of oxygen, hydrogen, and carbon, though the proportions of these substances have not been ascertained.

Malic acid combines with alkalies, earths, and metallic oxides, and forms salts known by the name of *malates*.

T is acid bears a strong resemblance to the citric, but differs from it in the following particulars:

1. The citric acid shoots into fine crystals, but this acid does not crystallize.

2. The salt formed from the citric acid with lime is almost insoluble in boiling water; whereas the salt made with malic acid and the same basis is readily soluble by boiling water.

3. Malic acid piecipitates mercury, lead, and silver, from the nitrous acid, and also the solution of gold when diluted with water; whereas citric acid does not alter any of these solutions.

4. Malic acid seems to have a less affinity than citric acid for lime; for when a solution of lime in the former acid is boiled one minute with a salt formed from volatile alkali and citric acid, a decomposition takes place, and the latter acid combines with the lime and is precipitated.

\* Scheele and Hermbstadt.

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## SECT. XVI.

#### OF SUBERIC ACID.

History.

CORK, a substance too well known to require any description, is the bark of a tree which bears the same name. By means of nitric acid, Brugnatelli converted it into an acid \*, which has been called the *suberic acid*, from *suber*, the Latin name of the cork tree. Several chemists affirmed that this acid was the oxalic, because it possesses several properties in common with it. These assertions induced Bouillon La Grange to undertake a set of experiments on suberic acid. These experiments, which have been published in the 23d volume of the *Annales de Chimie*, completely establish the peculiar nature of suberic acid, by showing that it possesses properties different from those of any other acid.

Preparation. 1. Suberic acid may be formed by pouring six parts of nitric acid of the specific gravity 1.261 on one part cork grated down, or simply broken down into small pieces, and distilling the mixture with a gentle heat as long as red vapours continue to escape. As the distillation advances, a yellow matter like wax makes its appearance on the surface of the liquid. While the matter contained in the retort is hot, it is to be poured into a glass vessel, placed upon a sand-bath over a gentle fire, and constantly stirred with a glass rod. By this

\* Crell's Annals, 1787.

#### SUBERIC.

means it becomes gradually thick. As soon as white vapours, exciting a tickling in the throat, begin to disengage themselves, the vessel is removed from the bath, and the mass continually stirred till it is almost cold.

By this means an orange-coloured mass is obtained of the consistence of honey, of a strong and sharp odour while hot, but having a peculiar aromatic smell when cold.

On this mass twice its weight of boiling water is to be poured, and heat applied till it becomes liquid; and then that part of it which is insoluble in water is to be separated by filtration. The filtered liquor becomes muddy; on cooling it deposits a powdery sediment, and a thin pellicle forms on its surface. The sediment is to be separated by filtration, and the liquor reduced to a dry mass by evaporating in a gentle heat. This mass is suberic acid. It is still a little coloured, owing to some accidental mixture, from which it may be purified either by saturating it with potash and precipitating it by means of an acid, or by boiling it along with charcoal powder.

2. Suberic acid thus obtained is not crystallizable, Properties. but when precipitated from potash by an acid it assumes the form of a powder; when obtained by evaporation it forms thin irregular pellicles.

3. Its taste is acid and slightly bitter; and when dissolved in a small quantity of boiling water it acts upon the throat, and excites coughing.

It reddens vegetable blues; and when dropt into a solution of indigo in sulphuric acid (liquid blue, as it is called in this country), it changes the colour of the solution, and renders it green.

Book II. Division II. 4. Water at the temperature of 60° or even 70° dissolves only  $\frac{1}{T_{T,\overline{0}}}$  part of its weight of suberic acid; and if the acid be very pure, only  $\frac{1}{T_{4,\overline{0}}}$  th part: boiling water, on the contrary, dissolves half its weight of it.

When exposed to the air, it attracts moisture, especially if it be impure.

5. When exposed to the light of day, it becomes at last brown; and this effect is produced much sooner by the direct rays of the sun.

When heated in a matrass, the acid sublimes, and the inside of the glass is surrounded with zones of different colours. If the sublimation be stopt at the proper time, the acid is obtained on the sides of the vessel in small points formed of concentric circles. When exposed to the heat of the blow-pipe on a spoon of platinum, it first melts, then becomes pulverulent, and at last sublimes entirely with a smell resembling that of distilled oil.

It is not altered by oxygen gas :---the other acids do not dissolve it completely. Alcohol developes an aro-matic odour, and an ether may be obtained by means of this acid.

It converts the blue colour of nitrate of copper to a green; the sulphate of copper also to a green; green sulphate of iron to a deep yellow; and sulphate of zinc to a golden yellow.

It has no action either on platinum, gold, or nickel; but it oxidizes silver, mercury, copper, lead, tin, iron, bismuth, arsenic, cobalt, zinc, antimony, manganese, and molybdenum.

6. With alkalies, earths, and metallic oxides, it forms compounds known by the name of *subcrates*.

# FORMIC.

# SECT. XVII.

# OF FORMIC ACID.

THIS acid is first mentioned in the Philosophical History, Transactions for 1671, in a paper by Mr Ray, giving an account of the observations of Mr Halse, and the experiments of Mr Fisher, on the acid juice which is spontaneously given out by ants, and which they yield when distilled \*. Mr Fisher compares this liquor with vinegar, but points out some differences between them. Scarcely any addition was made to these facts till Margraff published a dissertation on the subject in the Berlin Memoirs for 1749, in which he describes the method of obtaining the formic acid from the formica rufa, or red ant, and points out its properties with his usual precision and method +. A new dissertation was published on the same subject by Messrs Arvidson and Ochrn in 1782, in which the discoveries of Margraff were confirmed, and many new particulars added. Hermbstadt's paper on the same subject appeared in Crell's Annals for 1784. His researches were directed chiefly to the purification of the formic acid. He demonstrated that the juice of ants contained several foreign bodies, and among others, that a portion of malic acid might be detected in it. Richter published experiments on formic acid about the year 1793, pointing

# Plil. Trans. v. 2063.

+ Margraff's Opusc. i. 291.

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Chap. II.

# COMBUSTIBLE ACIDS.

Book II. Division II. out a method of procuring it in a very concentrated state \*. Deyeux soon after examined it, and found it analagous to the acetic acid +. This opinion of the French chemist was confirmed in 1802 by Fourcroy and Vauquelin who published a dissertation on ants, and concluded from their experiments, that the formic acid is nothing else than a mixture of the acetic and malic acids ‡. The opinion maintained by these celebrated philosophers induced Suersen to examine the subject by experiment. This chemist, in an elaborate dissertation on formic acid, published in 1805 6, shows that most of the facts pointed out by Fourcroy and Vauquelin had been already ascertained by preceding chemists ; that the experiments which they detail were not sufficient to warrant their conclusions; that formic acid when properly prepared contains no malic acid; and that it possesses properties different from the acetic. These conclusions have been farther confirmed by the experiments of Gehlen ||.

Frepara-

The simplest method of procuring formic acid in a state of purity is that of Margraff as corrected by Richter. Suersen accordingly had recourse to it. This method is as follows: Infuse any quantity of ants in about thrice their weight of water, put the mixture into a silver or tin coppered still, and draw off the water by distillation as long as it continues to come over without any burnt smell: for the distillation must be stop-

\* Gehlen, iv. 7.

+ Fourcroy, x. 491. Eng. trans. I have not seen either the dissertation of Richter or Deyeux.

- \$ Phil. Mag. XV. 148.
- || Ann. de Chim. 1x. 78,

S Gehlen's Jour. iv. I.

#### FORMIC.

ped as soon as that smell begins to be perceived. Satu- Chap. II. rate the water in the receiver with carbonate of potash, and evaporate to dryness. Mix the white mass thus obtained with as much sulphuric acid, previously diluted with its weight of water, as is sufficient to saturate the potash. Introduce the mixture into a retort, and distil slowly to dryness. The liquid which comes over into the receiver is to be again rectified by a very moderate heat, to get rid of any portion of sulphuric acid that may be present. It is now pure formic acid.

Formic acid thus procured is colourless like water. Properties, It cannot contain malic acid, because that acid cannot be distilled over along with water.

Its smell is peculiar, and very different from that of acetic acid. Its taste is acid. It reddens vegetable blues.

Its specific gravity varies from 1.102 to 1.113; whereas the most concentrated acetic acid is only 1.080.

It does not appear susceptible of being brought to the state of crystals; at least Lowitz attempted in vain to exhibit it in that state, though he succeeded readily with acetic acid.

Notwithstanding its greater specific gravity, it is capable of neutralizing much less of alkaline bodies than acetic acid, as appears from the following trials of Suersen. He reduced formic and acetic acids, each to the specific gravity 1.0525, and ascertained how much carbonate of potash, carbonate of lime, and carbonate of magnesia, the same weight of each of these liquids was capable of neutralizing. The result may be seen in the following little Table.

> Formic Acid. Acetic Acid. Magnesia ..... 150 ...... 213

# COMBUSTIBLE ACIDS.

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Analogy with acetic acid. Such are the differences between the formic and acetic acids pointed out by Suerson. In other respects there appears to be a striking analogy between the two acids.

Both of them form soluble compounds with all the alkalies and alkaline earths. They precipitate no metal from its solution, and of course form likewise soluble compounds with all the metallic oxides; but there is one striking difference pointed out long ago by Mr Fisher, which has not been noticed by any modern chemist. It is this: Acetate of lead when distilled yields no acid liquor whatever; but formic acid may be obtained from formate of lead precisely as acetic acid is procured from acetate of copper.

Upon the whole, though the experiments of the German chemists are sufficient to separate the formic and acetic acid, their analogy in other respects is so great, that farther researches are still requisite to elucidate the subject: Above all, an examination of the salts which the formic acid forms with the different bases ought to be undertaken, in order to ascertain whether formic acid may not be a combination of acetic acid with some unknown body. Gehlen indeed affirms that the formates differ from the acetates, and instances the formate of copper, which he says is a blue salt crystallizing in cubes.

# SECT. XVIII.

GENERAL REMARKS.

1. The preceding Sections of this Chapter contain an

account of all the acids at present known, except five ; which for obvious reasons have been referred to other parts of this Work. The first three of these will be described in the following Chapter. The other two, namely, the rosacic and amniotic, are never employed as instruments of analysis. Their acid characters are ambiguous, and their properties have been but imperfectly investigated. It appeared better, therefore, to reserve them till we came to treat of those animal substances in which they are found.

2. Several acids usually described by chemists will Acids denot be found in the preceding Sections, because their peculiar nature has been destroyed by the more precise investigation of modern analysis. The most remark. able of these acids are the five following.

# I. LACTIC ACID.

When milk is kept for some time it turns sour. Scheele examined the acid thus evolved, and gave it the name of lactic acid. He directs the following method of procuring it.

Evaporate a quantity of sour whey to an eighth Preparapart, and then filtrate it : this separates the cheesy part. Saturate the liquid with lime-water, and the phosphate of lime precipitates. Filtrate again, and dilute the liquid with three times its own bulk of water; then let fall into it oxalic acid, drop by drop, to precipitate the lime which it has dissolved from the lime-water; then add a very small quantity of limewater, to see whether too much oxalic acid has been added. If there has, oxalate of lime immediately presipitates. Evaporate the solution to the consistence of

tion.

Chap II. Acids omitted.

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honey, pour in a sufficient quantity of alcohol, and filtrate again; the acid passes through dissolved in the alcohol, but the sugar of milk and every other substance remains behind. Add to the solution a small quantity of water, and distil with a small heat; the alcohol passes over and leaves behind the lactic acid dissolved in water \*.

From the properties of the acid procured by this process, Scheele concluded that it was very analagous to the acetic, but that it wanted something to bring it

that state. He even pointed out a method of procuring vinegar from milk in considerable quantity, and ascertained that it always yielded a little when distilled  $\dagger$ .

From the recent experiments of Bouillon La Grange, we learn that the lactic acid is not a peculiar acid, but a mixture of the following substances: 1. Acetic acid; 2. Muriate of potash; 3. A little iron; and 4. An animal matter ‡.

# II. ZOONIC ACID.

WHEN animal substances and those vegetable principles which possess similar properties are distilled, the product contains an acid liquid, which Berthollet considered as peculiar, and called *zoonic* acid.

To obtain it, he mixed lime with the distilled liquid, evaporated nearly to dryness, then diluted and filtered.

• Scheele, Stockbolm Trans. 1780. 1 Ann, de Chim. 1. 288. † Scheele, ii. 66-

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Phosphoric acid was then added, and the mixture distilled. The receiver contained the zoonic acid \*.

From the more recent experiments of Thenard, we learn that this supposed acid is no other than the acetic, holding in solution a peculiar animal matter resembling oil +.

# III. Pyromucous Acid.

WHEN sugar and other sweet-tasted substances are distilled, among other products there is always a notable quantity of an acid liquid. This acid, when rectified, obtained the names of syrupous acid, and afterwards pyromucous acid. It is now known from the recent experiments of Fourcroy and Vauquelin, that this acid is nothing else than the acetic, holding in solution a portion of empyreumatic oil ‡.

# IV. & V. Pyrolignous and Pyrotartarous Acids.

WHEN wood is distilled in close vessels, it always yields more or less of an acid juice: the same remark applies to the salt called *tartar*. These liquids were distinguished by the name of *pyrolignous* and *pyrotartarous* acids: but they are now known to be only the acetic disguised by the presence of a peculiar oil §. It is proper to observe, however, that Gehlen has lately affirmed that the last of these acids is quite different

\* Ann. de Chim. xxvi. 86.

+ Ibid. xliii. 176.

‡ Ibid. xxxv. 131

§ Fourcroy and Vauquelin, Ann. de. Chim. xxxv. 131. Vol. II. Z Chap. II.

Book II. Division II. from the acetic. When cream of tartar is distilled, it yields an acid liquor, which, by proper concentration, deposites brownish crystals constituting an acid which cannot be acetic, and which differs equally from the tartaric \*.

3. The acids at present known, not reckoning those which remain to be described, amount to 34. Of these, one, the muriatic, possesses the characters of a simple substance; seven are products of combustion, and nine supporters of combustion. The remaining 17 are combustible. Oxygen is essential to the acidity of the products and supporters. The combustible acids almost all contain it; but it cannot be shown to be essential to their acidity. It has been usual with chemists to divide the combustible acids into vegetable and animal, because most of them are obtained from the vegetable and animal kingdoms. Several of the other acids have been denominated mineral for a similar reason.

4. Let us take a general view of all the acids, in order to ascertain in what degree each of them possesses those properties which are usually considered as characterising acid bodies. These properties are, 1. An acid taste; 2. The power of converting vegetable blues into red; 3. Solubility in water; 4. The property of forming salts.

Taste of the acids.

All the acids have a sour taste, except the *oxymuria*tic, the tungstic, the columbic, and the uric. In several the acidity is mixed, and even almost concealed, by some other more powerful taste. But this will be best understood by inspecting the following TABLE.

\* Ann. de Chim. 1x. 79.

Acids.	Taste.	Acids.	Taste.	Chap. II.
Tunstic Columbic Uric	None	Sulphuric Phosphoric Phosphorous Nitric	Acel	
Benzoic	Hot, acrid	Muriatic Fluoric	were a States	- 6
Oxymuriatic	Astringent	Acetic Oxalic	Acid, strong	1.471
Succinic Moroxylic	Acid, as- tringent	Tartaric Citric Kinic	and bed up.	
Arsenic Molybdic Chromic	Acid, me- tallic	Malic	Carbania Although	na asirs l
thing they part	Line and the second	Carbonic	ilessi differ a	anter and
Boracic Camphoric Suberic	Acid, bitter	Saclactic	Acid, weak	
Sulphurous	Acid, sulph.	Formic	asqui istroa dell'écution	

5. All the acids are destitute of smell excepting the following:

Acids.	Smell.	
Sulphurous	Sulphureous	
Phosphorous	Phosphureted hydrogen	
Muriatic.	ablition exclusion of TAN	
Fluoric	Muriatic acid	
Oxymuriatic	Aqua regia	
Hyperoxymuriatic	Nitrous gas	

Odour.

7. 2

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Acids.	Smell.
Nitric	
Acetic	Vinegar
Succinic *	Distilled nutgalls
Camphoric	Saffron
Benzoic * Moroxylic	Benzoin

Action on vegetable blues.

Carbonic acid, though a gas, has no smell whatever. 6. All the acids convert vegetable blues to red; but they differ exceedingly in the extent to which they possess this property. The greater number convert almost all vegetable blues (except indigo) to red; while some, the carbonic, for instance, only act upon the most delicate, as the tincture of turnsol. The cause of this change of colour has not been ascertained. In many cases it seems to be in consequence of the saturation of an alkaline or earthy substance which was previously combined with the colouring matter. This is the case evidently with respect to litmus. If this held always, the conversion of vegetable blues into red would be ' merely in consequence of the affinities between acids and alkaline bodies, and of the superior affinity which they have for them.

Solubility in water.

7. All the acids are soluble in water; but in this respect also they differ exceedingly from each other. Two of them are so soluble in water, that they have never

\*-In these two the odour is accidental, and owing to an oil.

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been obtained except in combination with that liquid. Chap. II.

# 1. Sulphuric, 2. Nitric,

The rest may be obtained either in the state of gas, or in a solid or crystallized form. Six of them are gases, which are readily absorbed by water to a certain amount; after which the water being saturated, refuses to absorb any more. The weight of each absorbed by 100 parts of water may be seen in the following TABLE.

- 2. Sulphurous..... 9.15
- 3. Carbonic..... 0'18
- 4. Oxymuriatic.....unknown
- 5. Hyperoxymuriatic ..... unknown
- 6. Fluoric.....unknown

The weight of the remaining acids, when solid or crystallized, soluble in 100 parts of water, is exhibited in the following TABLE.

Phosphoric Phosphorous Acetic Tartaric Malic	Very soluble, proportion not determined.	
Arsenic	152 parts	
Oxalic 50		
Boracic	1.6	
Saclactic	1.0	
Succinic 1.0		
Suberic 0.7		
Camphoric 0.5		

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Book H. Division II. All the acids are more or less soluble in alcohol, except phosphoric acid and the metallic acids. The sulphuric, nitric, and oxymuriatic, as we shall see afterwards, have the property of decomposing alcohol.

8. All the acids are capable of combining with alkalies, earths, and metallic oxides, and of forming with them compounds known by the name of salts. No substance which wants this property ought to be considered as an acid.

Combination with alkal es and earths.

Composition.

9. The two first classes of acids, as far as is known at present, are more simple than the third; as the acids belonging to them contain only two ingredients each, whereas the combustible acids contain three or even four constituent parts. These last are composed chiefly of oxygen, hydrogen, and carbon. Hence the reason that several of them may be converted into others by the action of nitric acid. This acid alters the proportion of their ingredients, either by abstracting part of their carbon and hydrogen, or by communicating oxygen, or by both together. But it is impossible to explain precisely what these changes actually amount to, without being acquainted with the component parts of every combustible acid, the manner in which these component parts are combined, and the affinities which exist between each of them. This, however, is very far from being the case at present. Though a vast number of experiments have been made on purpose to throw light on this very point, the difficulties which were to be encountered have been so great, that no accurate results have yet been obtained. All that is known at present is an approximation towards the component

parts of three acids. This may be seen in the follow- Chap. II.]

Acids.	Oxygen.	Carbon.	Hydrogen.
Acetic Oxalic	50.19	35.87	11.94
Tartaric	64 70.5	32 18	4 10.5

It was some time ago supposed by chemists, tha each of these acids was composed of a peculiar compound base or radical, combined with oxygen. The radical was supposed to be a combination of carbon and hydrogen; but no proof whatever has been given of the truth of this opinion, nor has the smallest evidence been produced that any such radicals exist. It is much more probable that all the ingredients of the acids are combined together, and constitute a triple combination.

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# OF COLORIFIC ACIDS.

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UNDER the name of colorific acids (till some more appropriate appellation occur), I include three substances, which possess such analogous properties that they ought to be classed together. As chemical bodies, they are all applied to nearly the same purposes; namely, to detect the presence of metallic bodies, and to separate, them from other substances. They act with great energy upon the metallic solutions, and at the same time precipitate them in powders remarkable for the intensity and variety of their colours. It was this circumstance that induced me to apply to them the epithet colorific.

Two of these bodies, namely, prussic and gallic acids, have been long considered as acids by chemists; though the second does not seem capable of neutralizing alkalies, and therefore is scarcely entitled to the name. A third of them, sulpbureted hydrogen, has been shown by Berthollet to act as an acid; but the compounds which it forms with alkalies are only transient. Its importance depends upon the energy with which it acts upon metallic bodies. Along with these three acids I class a fourth substance, tannin, which, though not an acid, is applied to the same purposes as the other

three. Indeed it would be difficult to assign any reason for giving the title of acid to gallic acid, which would exclude tannin. Upon the whole, perhaps, it would be better to distinguish these bodies altogether from the , acids, and to assign them a peculiar name of their own. In describing them, it may be proper to begin with the body in which the acid characters are best marked, and to terminate with that in which they can no longer be perceived. With this view they may be arranged in the following order : Comment is using strain in charming the

- The method of breis 1. Sulphureted hydrogen
  - 2. Prussic acid
  - 3. Gallic acid
    - 4. Tannin.

These bodies may be distinguished by the following characters :

1. They unite with alkaline bodies, but are all incapable of neutralizing them except the first; and the compound which it forms cannot be exposed to the air without decomposition.

2. They act with great energy upon metallic solutions, usually entering into combination with the oxide, and precipitating it in the state of an insoluble powder.

3. They have a tendency to enter into triple compounds with a variety of bodies, especially metallic oxides and alkalies; except the sulphureted hydrogen, which is commonly decomposed by metallic solutions.

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#### OF SULPHURETED HYDROGEN.

THIS substance forms the link by which the colorific acids are joined to the acids strictly so called. The Germans have given it the name of *bydrothionic acid*. The method of preparing this substance, and the most remarkable of its properties, have been detailed in a preceding part of this Work \*. As an instrument of chemical analysis it is usually employed in two states. 1. Dissolved in water; in which state it is called *liquid* sulphureted bydrogen. 2. Combined with alkalies, by causing a current of sulphureted hydrogen gas to pass through an alkaline solution till the liquid refuses to absorb any more. The liquid is then heated, to expel the excess of gas. In that state the compound is called an alkaline bydrosulphuret.

# SECT. II.

# OF PRUSSIC ACID.

Fintory.

WE are indebted to an accident for our knowledge of this important substance. About the year 1710 Dies-

\* See Vol. I. p. 89.

bach, a preparer of colours in Berlin, wishing to prepare some lake by precipitating a decoction of cochineal, alum, and green vitriol, with potash, borrowed some alkali for that purpose from Dippel. This chemist was the discoverer of a peculiar animal oil which goes by his name. He prepared it from blood; and the alkali with which he furnished Diesbach had been employed in the process. Instead of the red precipitate which he expected, a beautiful blue powder fell to the bottom. On mentioning the circumstance to Dippel, that chemist ascribed the formation of the powder to the action of his alkali on the alum and vitriol. It is not unlikely that he had calcined the potash together with a portion of blood. Be that as it may, he succeeded in discovering a method of procuring the blue powder at pleasure, and it was announced as a pigment in the Berlin Miscellanies for 1710. The preceding history, however, was only communicated to the public by Stahl 20 years after \*.

This powder was called Prussian blue; and the method of procuring it remained concealed, because it had become a lucrative article of commerce, till Dr Woodward published a process in the Philosophical Transactions for 1724, which he had procured, as he informs us, from one of his friends in Germany. This method was as follows: Detonate together four ounces Preparaof nitre and as much tartar, in order to procure an extemporaneous alkali; then add four ounces of dried bullock's blood ; mix the ingredients well together, and put them into a crucible covered with a lid, in which

tion.

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\* Stahl's Experimenta, Observat. Animadvers. ccc. numero. Chim. et Pbys. p. 281.

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there is a small hole; calcine with a moderate fire till the blood emits no more smoke or flame capable of blackening any white body exposed to it; increase the fire towards the end, so that the whole matter contained in the crucible shall be moderately but sensibly red. In this state throw it into four pounds of water, and boil it for half an hour. Decant off this water, and continue to pour on more till it come off insipid. Add all these liquids together, and boil them down to four pounds. Dissolve an ounce of sulphate of iron in half a pound of water, and eight ounces of alum in four pounds of boiling water: mix all the three solutions together while boiling hot. An effervescence takes place, and a powder is precipitated of a green colour. Separate this precipitate by filtration, and pour muriatic acid upon it till it becomes of a beautiful blue; then wash it with water and dry it \*.

Different explanations were given of the nature of this precipitate by different chemists. Mr Brown immediately repeated the process of Woodward, ascertained that other animal substances, as *beef*, may be substituted for blood; that the alum is useful only to dilute the colour; and that the blue pigment is produced by the action of the alkali (altered by blood) on the iron of the vitriol. He ascertained, too, that prussian blue is insoluble in muriatic acid, and that the green colour is owing to a mixture of prussian blue and oxide of iron, and that the muriatic acid developes the blue colour by dissolving the oxide of iron  $\dagger$ .

These facts were of considerable importance; but they

\* Pbil, Trans. xxxiii. 15.

+ Ibid. 1724. xxxiii. 17.

threw no light upon the theory of the process. An explanation of this was first attempted by Geoffroy, who had ascertained that any animal body whatever might be substituted for blood. According to him, the blood communicates a portion of inflammable matter, or phlogiston, to the alkali, and this inflammable matter revives the iron of the vitriol and brings it to the metallic state. A greater quantity of blood, by increasing the inflammable matter, will enable the alkali to revive still more of the iron, and thus to strike a blue at once, instead of a green \*. Though this explanation was approved of at the time by the best chemists, it was far from satisfactory +. Macquer soon after proceeded, by way of experiment, and added a new step to the facts ascertained by Brown.

That celebrated chemist ascertained the following Experifacts : 1. When an alkali is added to a solution of iron Macquer, in any acid, the iron is precipitated of a yellow colour, and soluble in acids; but if iron be precipitated from an acid by an alkali prepared by calcination with blood (which has been called a prussian alkali), it is of a green colour. 2. Acids dissolve only a part of this precipitate, and leave behind an insoluble powder which is of an intense blue colour. The green precipitate therefore is composed of two different substances, one of which is prussian blue. 3. The other is the brown or yellow oxide of iron ; and the green colour is owing to the mixture of the blue and yellow substances. 4. When heat is applied to this prussian blue, its blue colour is destroyed, and it becomes exactly similar to com-

\* Mem. Par. 1725. † Lewis, Neuman's Chem. p. 72..

ments of

Chap. III.

Book II. Division II. mon oxide of iron. It is composed therefore of iron and some other substance, which heat has the property of driving off. 5. If it be boiled with a pure alkali, it loses its blue colour also, and at the same time the alkali acquires the property of precipitating of a blue colour solutions of iron in acids, or it has become precisely the same with the prussian alkali. 6. Prussian blue, therefore, is composed of iron and something which a pure alkali can separate from it, something which has a greater affinity for alkali than for iron. 7. By boiling a quantity of alkali with prussian blue, it may be completely saturated with this something, which may be called colouring matter, and then possesses the properties of a neutral salt. 8. No acid can separate this colouring matter from iron after it is once united with it. 9. When iron dissolved in an acid is mixed with an alkali saturated with the colouring matter, a double decomposition takes place; the acid unites with the alkali, and the colouring matter with the iron, and forms prussian blue. 10. The reason that, in the common method of preparing prussian blue, a quantity of yellow oxide is precipitated, is, that there is not a sufficient quantity of colouring matter (for the alkali is never saturated with it) to saturate all the iron displaced by the alkali; a part of it therefore is mixed with prussian blue. Muriatic acid dissolves this oxide, carries it off, and leaves the blue in a state of purity .-- Such were the conclusions which Macquer drew from his experiments; experiments which not only discovered the composition of prussian blue, but threw a ray of light on the nature of affinities, which has contributed much towards the advancement of that important branch of chemistry.

The nature of the colouring matter, however, was still unknown. Macquer supposed it to be phlogiston. According to him, prussian blue is nothing else than iron supersaturated with phlogiston. This overdose protects the iron from acids, and prevents the magnet from acting on it. Heat drives off this dose, and leaves the prussian blue in the state of common iron\*. From this theory, which differed but little from that of Geoffroy, the alkali saturated with the colouring matter of prussian blue received the name of *pblogisticated alkali*. Macquer having observed that it did not act on alkaline and earthy solutions, while it precipitated all the metals, proposed it as an excellent *test* for detecting the presence of these last bodies.

The subsequent experiments of chemists threw an air of suspicion on Macquer's theory. Baumé ascertained, that when prussian blue is distilled, it always yields a portion of animal oil +; a product not very likely to appear if the powder contained nothing but phlogiston and iron. Deyeux and Parmentier, Bergman, Erxleben, Delius, and Scopoli, submitted prussian blue to distillation, and obtained a quantity of ammonia. Fontana ascertained that prussian blue detonated with nitre. Landriani obtained, by distillation, a little acid liquid and oil, and a great quantity of azotic gas and carbureted hydrogen gas. These facts were still more inconsistent, if possible, with Macquer's theory. Morveau advanced another in 1772; namely, that the phlogisticated alkali, besides phlogiston, contained also an acid which acted the principal part in the phe-

\* See Macquer's Dictionary, i. 177. + Baume's Chemistry, il. 601.

Chap. III.

Book II. Division II. nomena produced \*. Sage affirmed that the colouring matter in phlogisticated alkali was phosphoric acid; but this opinion was refuted by Lavoisier †. Bergman also announced his suspicions that it was an acid, but an unknown one ‡.

Such was the knowledge of chemists respecting the nature of this colouring matter, when Scheele all at once removed the veil, and explained its properties and composition. This he performed in two dissertations on prussian blue, published in the Stockholm Transactions for 1782 and 1783 ||.

He observed that the prussian alkali, after being exposed for some time to the air, lost the property of forming prussian blue; the colouring matter must therefore have left it.

He put a small quantity of it into a large glass globe, corked it up, and kept it some time; but no change was produced either in the air or the prussian alkali. Something must therefore displace the colouring matter when the alkali is exposed to the open air, which is not present in a glass vessel. Was it carbonic acid gas? To ascertain this, he put a quantity of prussian alkali into a glass globe filled with that gas, and in 24 hours the alkali was incapable of producing prussian blue. It is therefore carbonic acid gas which displaces the colouring matter. He repeated this experiment with this difference, that he hung in the globe a bit of paper which had been previously dipped into a solution of sulphate of iron, and on which he had let fall two drops

\* Digressions Academiques, p. 249.

‡ Notes on Scheffer, § 165.

† Mem. Par. 1777, p. 77. § Scheele, ii. 141.

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of an alkaline lixivium in order to precipitate the iron. Chap. III. This paper was taken out in two hours, and became covered with a fine blue on adding a little muriatic acid. Carbonic acid, then, has the property of separating the colouring matter from alkali without decomposing it.

He found also that other acids produce the same effect. Hence he concluded that the colouring matter might be obtained in a separate state. Accordingly he made a great many attempts to procure it in that state, and at last hit upon the following method, which suce signifizio. ceeds perfectly.

Mix together ten parts of prussian blue in powder, Preparas five parts of the red oxide of mercury, and thirty parts of water, and boil the mixture for some minutes in a glass vessel. The blue colour disappears, and the mix. ture becomes yellowish green. Pour it upon a filter; and after all the liquid part has passed, pour ten parts of hot water through the filter to wash the residuum completely. The oxide of mercury decomposes prussian blue, separates its colouring matter, and forms with it a salt soluble in water. The liquid therefore which has passed through the filter contains the colouring matter combined with mercury. The other component parts of the prussian blue being insoluble; do not pass through the filter. Pour this mercurial liquid. upon 21 parts of clean iron filings, quite free from rust. Add at the same time one part of concentrated sulphuric acid, and shake the mixture. The iron filings are dissolved, and the mercury formerly held in solution is precipitated in the metallic state. The cause of this sudden change is obvious: The iron deoxidizes the mercury, and is at the same instant dissolved by the sulphuric acid, which has a stronger affinity for it than Vol. II. Aa

Book II. Division II. the colouring matter has. There remains in solution therefore only sulphate of iron and the colouring matter.

> Now the colouring matter being volatile, which the sulphate of iron is not, it was easy to obtain it apart by distillation. Accordingly he distilled the mixture in a gentle heat: the colouring matter came over by the time that one-fourth of the liquor had passed into the receiver. It was mixed, however, with a small quantity of sulphuric acid; from which he separated it by distilling a second time over a quantity of carbonate of lime. The sulphuric acid combines with the lime and remains behind, which the colouring matter cannot do, because carbonic acid has a stronger affinity for lime than it has. Thus he obtained the colouring matter in a state of purity.

Composition.

It remained now to discover its component parts. He formed a very pure prussian blue, which he distilled, and increased the fire till the vessel became red. The small quantity of water which he had put into the receiver contained a portion of the blue colouring matter and of ammonia; and the air of the receiver consisted of azote, carbonic acid gas, and the colouring matter. He concluded from this and other experiments, that the colouring matter is a compound of ammonia and . oil. But when he attempted to verify this theory by combining together ammonia and oil, he could not succeed in forming colouring matter. This obliged him to change his opinion; and at last he concluded that the colouring matter is a compound of ammonia and charcoal. He mixed together equal quantities of pounded charcoal and potash, put the mixture into a crucible, and kept it red hot for a quarter of an hour; he then

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added a quantity of sal ammoniac in small pieces, which he pushed to the bottom of the melted mixture, kept it in the fire for two minutes till it had ceased to give out vapours of ammonia, and then threw it into a quantity of water. The solution possessed all the properties of the prussian alkali. Thus Mr Scheele succeeded in forming the colouring matter.

This colouring matter was called *prussic acid* by Morveau in the first volume of the chemical part of the *Encyclopedie Methodique*; an appellation which is now generally received, and which therefore it will be proper to employ in the remaining part of this Section.

These admirable experiments of Scheele were repeated and carried still farther by Berthollet in 1787; who applied to the explanation of the composition of the colouring matter the light which had resulted from his previous experiments on the component parts of ammonia. This illustrious chemist, not inferior to Scheele in ingenuity and address, ascertained, in the first place, that the phlogisticated alkali is a triple salt, composed of prussic acid; the alkali; and oxide of iron; that it may be obtained in octahedral crystals; and that when mixed with sulphuric acid, and exposed to the light, it lets fall a precipitate of prussian blue. His next object was to ascertain the component parts of prussic acid. When oxymuriatic acid is poured into prussic acid, obtained by Scheele's process, it loses its oxygen, and is converted into common muriatic acid. At the same time the prussic acid becomes more odorous and more volatile, less capable of combining with alkalies, and precipitates iron from its solutions, not blue, but green. Thus prussic acid, by combining with oxygen, acquires new properties, and is converted into a new substance,

Chap. III.

Book II. Division II. which may be called *oxy-prussic acid*. If more oxymuriatic acid gas be made to pass into prussic acid, and it be exposed to the light, the prussic acid separates from the water with which it was combined, and precipitates to the bottom in the form of an aromatic oil; which heat converts into a vapour insoluble in water, and incapable of combining with iron. When the green precipitate, composed of oxy-prussic acid and iron, is mixed with a pure fixed alkali, the oxy-prussic acid is decomposed, and converted into carbonate of ammonia.

From these experiments, Berthollet concluded, that prussic acid does not contain ammonia ready formed; but that it is a triple compound of carbon, hydrogen, and azote, in proportions which he was not able to ascertain. This conclusion has been still farther verified by Mr Clouet, who found, that when ammoniacal gas is made to pass through a red hot porcelain tube containing charcoal, a quantity of prussic acid is formed \*. This experiment does not succeed unless a pretty strong heat be applied to the tube  $\dagger$ .

Fourcroy and several other chemists believe, that the prussic acid contains also a portion of oxygen in its composition, resting chiefly upon an experiment of Vauquelin  $\pm$ . This is certainly possible, though it has not

\* Ann. de Chim. xi. 30.

+ Jour. de l'Ecole Polytechn. I. iii. 436.

‡ Vauquelin's experiments were as follows :

EXPER. I. Put into a retort IOO parts of the muriate of ammonia, 50 parts of lime, and 24 parts of charcoal in fine powder; adapt to the retort a receiver containing a slight solution of the sulphate of iron, and immerse into it the beak of the retort; then apply a brisk heat, and continue the action of the fire until nothing more is disengaged.

been proved; and the experiments of Berthollet render it somewhat unlikely.

Having thus traced the gradual progress of philosophers, in ascertaining the nature of the prussic acid, it only remains to give an account of its properties, which were first examined by the indefatigable Scheele.

Prussic acid obtained by Scheele's process is a co- Properties. lourless liquid like water. It has a strong odour, resembling that of the flowers of the peach, or of bitter almonds. Its taste is sweetish, acrid, and hot, and apt to excite cough. It does not alter the colour of vegetable blues. It is exceedingly noxious when taken in- Poisonous. ternally, even exposure to the fumes of it proves fatal to small animals. The poisonous qualities of the distilled water of bitter almonds and leaves of laurel are ascribed at present to this acid, which is known to exist in these waters in considerable quantity.

It is very volatile, and evidently capable of assuming Gaseous. the gaseous form ; though hitherto it has scarcely been examined in that state. The following experiment of

EXPER. 11. Put into a retort 100 parts of the muriate of ammonia, 50 parts of semi-vitreous oxide of lead, and 25 parts of charcoal; adapt a receiver containing a solution of sulphate of iron, and proceed as before. Stir well the liquors contained in the receivers, and expose them to the air for several days, in order that the combination between the oxide of iron and the prussic acid may be perfect, and that the prussiate of iron may absorb as much oxygen as is necessary for its passing to the state of blue prussiate, and for its being proof against acids: then pour into these liquors equal quantities of sulphuric acid well diluted with water, and you will have prussian blue, the quantities of which will be as one to six ; that is to say, the prussian blue of the experiment in which Vauquelin employed oxide of lead, was six times more abundant than that of the experiment in which he employed only lime to discogage the ammonia.

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Not readily acted on by

heat.

Grindel, if accurate, shows that it may be procured in gas. He put a quantity of prussian blue into a glass flask, and fitting to it a bent tube, applied the heat of a lamp; as soon as the smell of bitter almonds became perceptible, the tube was plunged under mercury, and the gas evolved received in a jar containing liquid potash. The gas was absorbed by the potash, and the liquid, on being evaporated, deposited crystals, which possessed all the properties of prussiate of potash \*.

From the recent experiments of Richter and Bucholz, we learn that this acid is capable of resisting a much more violent heat without decomposition, than any of the vegetable acids. It is formed only when the potash and blood are exposed to a red heat. When united to potash, a considerable heat may be applied to the combination without occasioning decomposition; but when the salt is dissolved in water prussic acid is immediately disengaged, as is evident by the odour of bitter almonds evolved ; while at the same time a portion of ammonia and of carbonic acid is formed. Thus we see that water destroys the combination of this acid and alkalies. Bucholz supposes that the effect is produced by the mutual action of the acid and water which decompose each other t. These facts explain the reason of the facility with which the alkaline prussiates are decomposed by mere exposure to the air, and by all the acids, and show us that they can scarcely be applied to any useful purpose in chemistry, even if their difficult formation did not present an unsurmountable bar to their introduction.

\* Phil. Mag. xviii, 151.

† Gehlen's Jour. i. 406.

# PRUSSIC.

The presence of a metallic oxide serves to fix the constituents of prussic acid, and to prevent them from being acted upon by water or any other body. Hence those salts into which a metallic oxide enters are much more permanent in their nature, and of course may be used for chemical purposes.

Prussic acid then may be prepared as a reagent in four states : 1. In a state of purity, either gaseous or dissolved in water. 2. United to alkalies. 3. United to alkalies and metallic oxides at once in the state of a neutral salt. 4. United to metallic oxides alone.

1st, In the state of prussic acid its action on metallic Action on solutions is but feeble. Of all the metallic solutions tried by Scheele, pure prussic acid occasioned only a precipitate in three : namely,

1. Nitrate of silver precipitated white.

2. Nitrate of mercury ..... black.

3. Carbonate of iron..... green becoming blue. It has no action on the oxides of

1. Platinum,	4. Lead,	7. Manganese,
2. Iron,	.5. Bismuth,	8. Arsenic,
	And the second second second	

6. Antimony, 9. Molybdenum. 3. Tin, 10. Gold precipitated by the alkaline carbonates is rendered white by this acid.

11. It disengages carbonic acid from the oxide of silver, precipitated by the same alkalies; but the oxide remains white.

12. It dissolves red oxide of mercury, and forms with it a salt which may be obtained in crystals.

13. Oxide of copper precipitated by carbonate of potash effervesces in it, and acquires a slight orange-yellow colour.

14. Oxide of iron precipitated from the sulphate of

metals.

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iron by carbonate of potash, effervesces in it, and becomes blue.

15. Oxide of cobalt precipitated by the same alkali, gives in it some marks of effervescence, and becomes yellowish brown \*.

2d, From the experiments of Scheele, Richter, and Bucholz, we learn, that the alkaline prussiates act with sufficient force upon metallic solutions, and produce more beautiful precipitates than the triple prussiates; but, for the reasons already assigned, they cannot be introduced into use with advantage.

3d, As the triple prussiates are usually prepared by digesting alkaline bodies on prussian blue, the oxide of iron is the metallic body which enters into combination with the acid and base, and constitutes the compound a triple salt. Potash has, with one consent, been adopted by chemists as most convenient; but other alkaline bodies would doubtless answer equally well. *Ferruginous prussiate of potash*, then, is the substance usually employed as a reagent. It is a yellow-coloured salt which crystallizes in flat cubes. It is used to detect the presence of metallic bodies by the colour of the precipitate formed, and in an especial manner to detect iron, which it does by the blue colour that the solution assumes; and to free solutions from iron, which it does by precipitating the iron in the form of prussian blue.

Ferruginous prussiate of potash.

Prussiate of mercury.

4tb, The only soluble combination of prussic acid and a metallic oxide is prussiate of mercury: the method of obtaining which is described above. It is a white salt of a disagreeable metallic taste, crystallizes in

\* Scheele, ii. 169.

# GALLIC.

needles, and forms a colourless solution in water. This salt is employed with great advantage in several cases. By means of it, for example, Dr Wollaston has pointed out a method of separating palladium with facility from crude platina. Dissolve crude platina in nitro-muriatic acid; throw down the platinum with sal ammoniac, neutralize the remaining solution with an alkali, and then drop in prussiate of mercury; a yellow precipitate gradually forms, which, when heated to redness, leaves pure palladium.

The only earthy bodies precipitated by the prussiates are zirconia and yttria. This property distinguishes these two earths from all the rest, and points out an analogy between them and the metallic oxides.

# SECT. III.

# OF GALLIC ACID.

THERE is an excrescence, known by the name of nut- History gall, which grows on some species of oaks. This substance contains a peculiar acid, called from that circumstance gallic acid ; the properties of which were first examined with attention by the commissioners of the Academy of Dijon, and the result of their experiments was published in 1777, in the third volume of their Elements of Chemistry \*. In these experiments, however, they employed the infusion of galls, in which the

\* Vol. III, p. 403.

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Book II. Division II. Pr. paration. acid is combined with tannin. It was reserved for Scheele to obtain it nearly in a state of purity.

1. He observed, in an infusion of galls made with cold water, a sed ment, which proved on examination to have a crystalline form and an acid taste. By letting an infusion of galls remain a long time exposed to the air, and removing now and then the mouldy skin which formed on its surface, a large quantity of this sediment was obtained; which being edulcorated with cold water, redissolved in hot water, filtrated and evaporated very slowly, yielded an acid salt in crystals as fine as sand \*.

Deyenx has proposed a much speedier method of obtaining gallic acid +; but it does not succeed without a good deal of precaution. It consists in exposing pounded nut-galls in a large glass retort to a heat cautiously and slowly raised. A number of brilliant white crystalline plates are sublimed, which possess all the properties of gallic acid. Care must be taken not to apply too great a heat, and to stop the process before any oil begins to come over, otherwise the crystals will be redissolved, and the whole labour lost.

Mr Davy has lately pointed out another method which yields gallic acid in a state of considerable purity. Boil for some time a mixture of carbonate of barytes and infusion of nut-galls. A bluish green liquid is obtained, which consists of a solution of gallic acid

\* Stockholm Trans. 1786 — The crystals obtained by this method always contain a portion of tannin, and are of a brown colour.

+ This method was in fact discovered by Scheele; but Deyeux repeated it, and pointed out the proper precautions.—See Crell's Annals, i. 29. Eng. Transl.

and barytes. Filter and saturate with diluted sulphu- Chap. III. ric acid. Sulphate of barytes is deposited in the state of an insoluble powder, and a colourless solution of gallic acid remains behind \*.

Many other processes besides these have been proposed by different chemists, but as they are all liable to considerable objections, it is not necessary to enumerate them. The following method proposed by Richter, though expensive and tedious, is one of the best :

" Infuse in cold water one pound and a half of gall. Method of nuts, previously reduced to fine powder, taking care frequently to agitate the mixture. Pass the liquid through a cloth; add water to the pulp which refuses to go through, and again put it through the cloth, using a press to separate the water. Join the liquors, and with a gentle heat evaporate them, and a matter of a dark brown colour, and very brittle, will be obtained.

" Pure alcohol poured on this matter, reduced to a fine powder, acquires a pale straw colour. The deposite infused again in alcohol communicates but little colour to it. The brown residuum now left is composed almost wholly of pure tannin. Mix the two alcoholic extracts, which distil in a small retort to one eighth. What remains will be almost a solid mass. Pour water on it, and expose it to a gentle heat, and you will obtain a clear and almost colourless solution.

" Evaporate this solution, and you will obtain from it very small, white, prismatic crystals. The liquor furnishes more, but they are commonly a little coloured. It is sufficient to levigate them with water to ob

\* Journal of the Royal Instit. i. 274;

Richter.

Book II. Division II: tain them very white. By this process half an ounce of crystals is procured from one pound of galls; these crystals are extremely light, and consequently occupy a considerable space \*."

Method of Proust.

The method of Scheele is by far the cheapest; but it never yields a pure acid. Mr Proust has proposed the following method of remedying this defect : Form a strong infusion of galls, set it aside till impure crystals of gallic acid are deposited. Dissolve these crystals in water, and drop muriate of tin cautiously into the solution. Flocculi are deposited, and the solution becomes clear. Filter and evaporate. Pure crystals of gallic acid are deposited, which require only to be dried upon blotting paper +. I have tried this method of Proust, but it did not succeed. Berthollet has proposed as a substitute to heat this solution of gallic acid with recently precipitated oxide of tin. But this method likewise failed in the hands of Bouillon La Grange, who has lately published a dissertation on gallic acid, and endeavoured to prove that it is merely acetic acid combined with tannin and extractive. But his proofs are not sufficiently conclusive. He has shown, however, that nutgalls contain acetic acid, and that the different gallates, when decomposed by sulphuric acid, emit the odour of acetic acid t.

Properties.

2. Gallic acid, when pure, is in the form of transparent plates or octahedrons. Its taste is acid, and somewhat astringent; and when heated it has a peculiar and rather unpleasant aromatic odour.

> \* Phil. Mag. xxiii. 74. ‡ Ann. de Chim. 1x. 156.

+ Jour. de Poys. 1xi. 117.

3. It is soluble in  $1\frac{1}{2}$  parts of boiling water, and in 12 parts of cold water. When this solution is heated, Solubility. the acid undergoes a very speedy decomposition. Alcohol dissolves one-fourth of its weight of this acid at the temperature of the atmosphere. When boiling hot, it dissolves a quantity equal to its own weight. It is soluble also in ether.

4. When exposed to the action of heat, it is sublimed, Action of but its properties are somewhat altered, as Bouillon La Grange has shown. In like manner the acid sublimed by Deyeux's process differs in its properties from the crystallized acid of Scheele and Richter. Deyeux announced, that when the gallic acid is distilled it yields oxygen gas. When Berthollet repeated the experiment he obtained only carbonic acid. Bouillon La Grange has shown, that besides the carbonic acid, there comes over likewise a portion of heavy inflammable air, and that water is formed. By repeated distillations the whole acid may be decomposed and converted into these products. Hence it is obvious that gallic acid, like most of the other combustible acids is composed of oxygen, hydrogen, and carbon. The proportion of carbon, if we judge from the quantity of carbonic acid evolved, must be very considerable.

5. Gallic acid in crystals is not altered by exposure Action of to the air. Neither oxygen gas, the simple combustibles, nor azote, seem to have any particular action on it. Its action on the metals has not been examined. When the solution of this acid in water is exposed to the air, it gradually acquires a brown colour, and the acid is destroyed; the surface of the liquid becoming covered with mouldiness.

6. It combines with alkaline bodies, separating the

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Action on earths. carbonic acid if they were in the state of carbonates. The compounds formed have received the name of gallates; but hitherto have scarcely been examined.

7. In alkaline solutions it occasions no deposite, but when dropt into barytes water, strontian water, or lime water, it gives them a bluish-red colour, and occasions a flaky precipitate, composed of the acid combined with the earths \*.

Gallic acid occasions a precipitate when poured into solutions of glucina, yttria, and zirconia in acids. This property distinguishes these three bodies from all the other earths, none of which are precipitated from their solutions in acids by gallic acid +.

On metals.

8. Upon the metallic solutions it acts with considerable energy, changing the colour, and producing precipitates in many of them. Hence it is frequently used as a reagent to detect the presence of metallic bodies; but the difficulty of freeing it sufficiently from tannin renders it scarcely safe to trust the experiments hitherto made on that point. Richter has shown, that it is not capable of taking iron from sulphuric acid, as has been hitherto supposed, unless it be assisted by the action of some other body which has an affinity for sulphuric acid. He has endeavoured to show, too, contrary to the experiments of Proust, that it strikes a black with all the oxides of iron. Berthollet has more lately employed his ingenuity to establish the same doctrines,

\* It is not unlikely that these precipitates are occasioned by the presence of a little tannin, and that they would disappear if the acid were pure.

+ If we except their solutions in carbonic acid. Alumina is precipitated from acids by infusion of nut-galls, but not immediately.

## TANNIN.

but has by no means silenced Proust, who has published experiments apparently decisive.

When it precipitates metallic oxides, gallic acid appears to act by bringing them nearer to the state of metals, and some of them, as gold, are completely reduced.

SECT. IV.

## OF TANNIN.

NUTGALLS contain several other ingredients besides gallic acid; but one of the most remarkable and important is the substance called *tannin*, which will occupy our attention in this Section.

The first attempt at a regular examination of the properties of nutgalls was made by Dr Lewis, during a set of experiments undertaken to ascertain the best mode of making ink \*. He detected in them a substance which precipitates black  $\dagger$  with the oxides of iron, and coagulates with isinglass  $\ddagger$ ; but chemistry in his time had not made sufficient progress to enable him either to separate or examine this substance. Deyeux was perhaps the first chemist who ascertained the peculiar nature of *temnin*. He pointed it out in his analysis of nutgalls as a peculiar resinous substance, but withont assigning it any name §. Seguin soon after engaged in a set of experiments on the art of tanning leather || \*

 History.

Book II. Division II. during which he discovered that *tannin* has the property of precipitating glue from its solutions in water, and of combining with the skins of animals. This led him to suppose it the essential constituent of the liquids employed for the purpose of tanning leather. Hence the names *tannin* and *tanning principle* given it by the French chemists; but it is to Mr Proust that we are indebted for the first investigation of the nature and properties of tannin, and of the methods of obtaining it in a separate state \*. Much curious and important information has likewise been obtained by the experiments of Mr Davy on the constituent parts of astringent vegetables, and on their operation in tanning<sup>‡</sup>. Fiedler<sup>‡</sup>, Richter §, and Merat Guillot ||, have also published interesting experiments on this difficult subject.

An elaborate dissertation on tannin was published by Trommsdorf in the summer of  $1804 \P$ ; in which he analysed the opinions of Proust, and examined the properties of tannin with his usual industry. Many of his conclusions had been anticipated by Davy, whose labours, however, they serve to corroborate and confirm; but the recent labours of Mr Hatchett have formed a new era in the history of tannin. This sagacious philosopher, during a set of experiments on resins and bitumens, discovered a method of forming tannin artificially from almost every animal and vegetable body, and thus furnished chemists with the means of procuring it with facility in a state of purity. His disserta-

\* Ann. de Chim. xxv. 225.--xxxv. 32,--and xlii. 89. + Phil. Trans. 1803, p. 233. and Jour. of the Royal Instit. vol. ii. \$ Jour. de Chim. i. 86. § Ibid. iii. 307. and 334.

Ann. de Chimi xli. 323.

Gehlen's Jour. iii. 111,

## TANNIN.

tions on an artificial tanning substance were read to the Royal Society in the summer of 1805.

These discoveries will make it proper for us to divide this subject into two parts. We are now in possession of two kinds of taunin; one kind formed in plants by the processes of vegetation ; another formed artificially by the methods pointed out by Mr Hatchett: each of these appears capable of assuming different modifications, either from slight alterations in the constituents, or from the combination of small portions of foreign bodies.

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tion, which children overslow oversorium 195 states of

1. TANNIN exists in a great number of vegetable substances; but it may be procured most readily and in the greatest purity from nutgalls and catechu.

NUTGALLS are excrescences formed on the leaves of Preparathe oak by the puncture of an insect which deposits its eggs on them. The best are known by the name of Aleppo galls, imported in large quantities into this country for the use of the dyers, calico-printers, &c. They are hard like wood, round, often nodulated on the surface, of a bluish colour, and an excessively disagreeable taste. They are in a great measure soluble in water ; what remains behind is tasteless, and possesses the properties of the fibre of wood. A very great proportion of water is necessary to carry off every thing soluble. Deyeux found, that a French pound of nutgalls. required 96 French pints of water, applied in 20 different portions one after the other, and allowed to mace. Vol. IT. Bb

tion from nutgalls,

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Book II. Division II. Division II. standard, gives us about 150 English pints to a pound troy of nutgalls. But Trommsdorf exhausted the soluble part of nutgalls, by means of 40 times their weight of water, applied in three successive portions, each continuing two days on the galls, at the temperature of 66°<sup>+</sup>.

> From the analyses of Deyeux and Davy, it follows, that the soluble part of nutgalls consists chiefly of five ingredients; namely, tannin, extractive, mucilage ‡, gallic acid, and gallate of lime. Mr Davy found that 500 grains of Aleppo galls formed with water a solution, which yielded by slow evaporation 185 grains of matter. This matter he found composed of

> > 130 tannin

31 gallic acid and extract

12 mucilage and extract

12 lime and saline matter

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So that the tannin constitutes rather more than two-thirds of the whole.

2. No fewer than five methods have been proposed to separate tan from the infusion of nutgalls, and procure it in a state of purity; but none of them answers the purpose completely.

First. When a solution of muriate of tin is dropped into the infusion of nutgalls, a copious yellow precipitate immediately falls; which, when separated by fil-

\* Ann. de Chim. xvii. 12.

+ Gehlen's Jour. iii. 113.

‡ Extractive and mucilage are vegetable substances, which will be treated of in a subsequent part of this Work.

§ Phil. Trans. 1803, 251.

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Prepara-

tion.

tration and dried, assumes the appearance of a buff-coloured light powder. According to Mr Proust, who first examined this powder, it is a compound of oxide of tin and tannin. If it be mixed with water, and a current of sulphureted hydrogen gas passed through it, sulphuret of tin is formed, which remains insoluble; and the tannin, as it is separated from the oxide, dissolves in the water. This water, when freed from the sulphuret by filtration, and evaporated to dryness. leaves a brown coloured substance, which Proust considered at first as pure tannin\*. But as the infusion of nutgalls contains a portion of extract, which is likewise precipitated by muriate of tin, it is obvious, that by this process we do not obtain pure tannin, but a combination of tannin and extract. Neither is the whole of the tannin precipitated; a portion of it combined with the oxide remaining in solution, unless thrown down by an alkali +. Mr Davy has rendered it probable that this precipitate contains also muriatic acid ‡. From these facts it is obvious that pure tannin is not obtained by this process.

Second, When the infusion of nutgalls, somewhat concentrated by evaporation, is mixed with a saturated solution of carbonate of potash, a yellowish-white matter precipitates abundantly in the form of flakes. When this precipitate is dried, it assumes the form of a whitish powder, which was first examined by Deyeux, to whom we are indebted for the process §. Proust considers this precipitate as pure *tannin*; and accordingly

\* Ann. de Chim. XXV. 226. \$ Phil. Trans. 1803, p. 249. † Proust, Ann. de Chim. xlii. 89. § Ann. de Chim. xvii. 19. B b 2 387

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proposes this process as one of the easiest for procuring that substance from the infusion of nutgalls. According to him, carbonate of potash has a stronger affinity for water than tannin. Hence the reason that it occasions its precipitation \*. But this conclusion is by no means consistent with the properties of the precipitate ascertained by Deyeux, and is altogether inconsistent with the properties ascertained by Davy. Its colour is white; it is nearly tasteless; it is not completely soluble in water; when heated, it yields crystals of gallic Mr Davy has shown that it consists chiefly of acid. tannin and gallic acid combined with the carbonates of potash and lime t. The results obtained by Davy are confirmed likewise by the subsequent experiments of Trommsdorf ‡. This method, of course, does not yield pure tannin.

Third. When concentrated sulphuric or muriatic acid is dropt into a strong infusion of nutgalls, a white curdy precipitate immediately falls. This fact was first observed by Dizé §. According to Proust, the precipitate is a compound of tannin and the acid employed. If we wash it with cold water, dissolve it in boiling water, and saturate the acid with carbonate of potash, the tannin, according to him, separates in a state of purity. It may be washed with cold water and dried  $\parallel_{e}$ But besides tannin extract must be present in this preeipitate; for it is well known that it is thrown down by sulphuric acid. Mr Davy has rendered it probable that it contains also some gallic acid. By distilling it

\* Ann. de Chim. XXXV. 32. ‡ Gehlen's Jour. iii. 117. || Ibid. p. 37. + Phil. Trans. 1803. 245. § Ann. de Chim. XXIV. 37in a heat above 212°, he obtained a yellowish coloured liquid, which gave a black colour to oxysulphate of iron, though it formed no precipitate with gelatine; it therefore contained gallic acid\*. Trommsdorf's experiments show us likewise that this method does not yield pure tannin <sup>‡</sup>.

Fourth. If lime-water be mixed with an infusion of nutgalls, a copious precipitate falls. When this precipitate is treated with diluted nitric or muriatic acid, an effervescence takes place, the liquid becomes deep coloured; and when filtrated leaves behind it a substance of a brilliant black colour, which Merat-Guillot, to whom we are indebted for this process, considers as pure tannin<sup>‡</sup>. But Mr Davy has shown that it must also contain the extractive matter, which is thrown down in combination with lime as well as the tannin §. The effervescence indicates sufficiently the presence of carbonic acid; a proof that the precipitate is even still more complicated. This method, then, is scarcely preferable to the former.

Fifth. The process practised by Trommsdorf, though not unexceptionable, appears to yield tannin in a state of greater purity than any other hitherto thought of. It is as follows: Three parts of nutgalls were reduced to powder, and digested with 40 parts of water for three days, at the temperature of 66°, the mixture being frequently stirred. The whole was now passed through a linen strainer, the liquid set apart, and the powdered nutgalls remaining on the strainer were treated as before with 40 parts of water. This digestion with fresh

\* Phil. Trans. 1803. 240. ‡ Ann. de Chim. xli. 323. + Gehlen's Jour. iii. 127. § Pbil. Trans. 1803. 262.

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water was continued till four different infusions in all had been drawn off the nutgalls. The last of these was colourless, and produced no change upon the solution of iron. These infusions were mixed together, and evaporated gently down to one fourth in a porcelain basin. The liquid being now muddy was passed through a thick linen cloth, by means of which a quantity of extractive was separated. The whole was then evaporated to the consistence of a jelly, and placed upon a flat porcelain dish near a stove till it became quite dry. The brown coloured substance thus obtained was digested with thrice its weight of *pure* alcohol \*; and this digestion was repeated in all three times, till the last portion of alcohol was found to contain no trace of gallic acid. In order to make sure of removing the gallic acid, the dry residue was digested twice successively with alcohol containing ten per cent. of water. It was now considered as tannin in a considerable degree pure, but still contaminated with some extractive and mucilaginous matter. To get rid of these, the whole was dissolved in distilled water, and repeatedly evaporated to dryness, in hopes of rendering the extractive insoluble; but nothing was separated by this process. When the solution was left for some time in a warm place, a mould collected on the surface, which was removed, and ascribed to a portion of mucilage which had been present. The solution being now filtered, and evaporated to dryness. left a residue consisting of tannin in a state of considerable purity, but still contaminated with a quantity of sulphate of lime. To get rid of this salt, Mr Tromms-

\* Alcohol of the specific gravity 0.796 is at present considered as pure, or free from water dorf employed the following method : The tannin was dissolved in water, and carbonate of potash dropt in as long as any precipitate fell. The liquid was separated from this precipitate by filtration, and mixed with acetate of lead. A powder fell, consisting of the oxide of lead combined with tannin. This powder was washed and dried; and being mixed with water, a current of sulphureted hydrogen was passed through. By this means the lead was separated and remained in combination with sulphur, while the tannin dissolved in the water. The liquid being now filtered, boiled, and evaporated to dryness, left a residue, which may be considered as tannin in a state of as great purity as it can be procured from nutgalls \*.

3. CATECHU, or terra japonica as it is also called, is From catea substance obtained by decoction and evaporation from a species of mimosa which abounds in India. It has a reddish brown colour, an astringent taste, leaving an impression of sweetness; it is not altered by exposure to the air. There are two varieties of it; one from Bombay, which has the lightest colour, and a specific gravity of 1.39; and one from Bengal, which is of the colour of chocolate ; its specific gravity is 1.28 +. This substance was examined by Davy, and found to consist chiefly of tannin combined with a peculiar species of extractive. If the darkest parts of the catechu be selected, and infused in cold distilled water for a short time, the infusion, when evaporated to dryness, consists of tannin combined with a very minute quantity of extract. It may therefore be employed to ascertain the properties of tannin.

> \* Gehlen, iii. 113, and 124. + Davy, Ibid. 252.

chu.

Chap. 111.

Book II. Division II. Properties. 4. Tannin procured from nutgalls by Trommsdorf's method, is a substance of a brown colour, brittle, and breaking with a resinous fracture. Its taste is bitter and very astringent, like that of nutgalls.

It dissolves readily in water, both hot and cold, and forms a solution of a brown colour, which, from Trommsdorf's experiments, does not seem liable to become mouldy, nor to undergo a spontaneous decomposition when exposed to the air in a moderate heat.

Insoluble in alcohol. Pure alcohol does not dissolve tannin; but it is readily soluble in alcohol diluted with water, even though the portion of water be but small. Thus alcohol, of the specific gravity 0.818, dissolves it, though it contains, according to Lowitz's table, only  $\frac{1}{10}$ th of water. These important facts seem first to have been observed by Richter, and to have furnished him with the method formerly described, of procuring gallic acid in a state of purity.

Action of oxygen.

5. From the experiments of Proust, Davy, and Deyeux, we learn that it is capable of combining with oxygen; but at the same time it is either decomposed altogether, or its nature completely altered. Thus nitric acid converts it into a yellowish brown matter soluble in alcohol, and similar in its properties to an extract\*. Oxymúriatic acid produces similar effects; and Mr Proust has observed, that the peroxide of tin changes it also into an extract<sup>+</sup>, perhaps by communicating oxygen.

6. The action of the simple combustibles on tannin has not been examined.

\* Davy, P.il. Trans. 1803, 241.

+ Ann. de Chim. xlii. 931

7. The action of the metals upon tannin does not Chap. III. seem to be great; but almost all the metallic oxides have an affinity for it, and are capable of combining with it; the compound is usually nearly insoluble in water. Hence the reason why the infusion of nutgalls precipitates metallic solutions so readily. These compounds have been hitherto in a great measure overlooked by chemists. The following observations contain the facts at present known.

When the peroxide of tin or zinc is boiled in the infusion of galls, it acquires a dull yellow colour, and abstracts all the constituents from the infusion, leaving behind only pure water. The oxides thus combined with tannin, &c. are partly soluble in muriatic acid. and the solution indicates the presence of tannin and gallic acid \*. When peroxide of tin is allowed to act upon the cold infusion, it abstracts all its constituents in a few days; but Mr Proust + affirms, that in that case the gallic acid is mostly destroyed, and a portion of the tannin brought to the state of extractive.

When the metallic salts are mixed with the infusion of galls, the precipitate consists of the metallic oxide combined with the tannin, the extract, and the acid of the infusion; and, according to Davy, it contains also a portion of the acid of the metallic salt ‡.

Tannin does not seem to produce any change upon the solution of sulphate of iron : but when it is mixed with a solution of the oxysulphate of iron, a deep blue coloured precipitate immediately appears, consisting of

\* Davy, Phil. Trans. 1803, 244. + Ann. de Clim. xlii. 92. \$ Phil. Iraas. 1803, 248.

Action of metallic oxides

Book II. Division II.

the tannin combined with the oxide. This precipitate, when dried, assumes a black colour. It is decomposed by acids.

When too great a proportion of oxysulphate of iron is poured into a solution of tannin, the sulphuric acid, set at liberty by the combination of the iron and tannin, is sufficient to re-dissolve the precipitate as it appears; but the precipitate may easily be obtained by cautiously saturating this excess of acid with potash. When the experiment is performed in this manner, all the oxysulphate of iron which remains in the solution undecomposed is converted into sulphate. Mr Proust supposes that this change is produced by the tannin absorbing oxygen from the iron.

Tannin combines with gelatine.

8. One of the most important properties of tannin is the insoluble compound which it forms with glue or gelatine, as this substance is termed by chemists. It is therefore employed to detect the presence of gelatine in animal fluids; and, on the other hand, solutions of gelatine are employed to detect the presence of tannin in vegetable fluids, and to ascertain its quantity. Now although the compound of gelatine and tannin is insoluble in water, it is soluble both in the solution of tannin and of gelatine when sufficiently diluted. It is necessary, therefore, that the solution of gelatine, used to detect tannin, should be as concentrated as is consistent with its perfect fluidity; for glue, when gelatinous, does not act upon tannin. It is necessary also that it should be employed quite fresh; for when in a state of putrefaction, it loses its property of precipitating tannin\*.

\* I find that even the addition of as much alcohol as is consistent with the gelatine remaining in solution, does not preserve it in a proper state for use.

#### TANNIN.

Mr Davy has ascertained, that the best proportion for Chap. III. use is a solution of 120 grains of isinglass \* in 20 ounces of water. Care must be taken not to add an excess of the solution to the liquid from which the tannin is to be separated; because the compound of tannin and gelatine is re-dissolved by the solution of gelatine. According to the analysis of Mr Davy, this compound, when dried in the temperature of 150°, is composed of

> 54 gelatine 46 tannin

# 100+

9. Potash and soda combine with tannin, and form Action of with it a compound less soluble in water than pure tannin, and which does not precipitate glue till the alkali, is saturated with an acid ‡. Ammonia produces the same effects. The fixed alkalies occasion a precipitate in concentrated solutions of tannin, but ammonia throws down nothing §.

When potash or soda is added to the infusion of nutgalls, the liquid assumes a reddish-brown colour, and loses the property of precipitating gelatine till the alkali is saturated with an acid. When the alkalized infusion is evaporated to dryness, an olive coloured mass remains, of a faint alkaline taste, which deliquesces in the air. Ammonia produces the same effect upon the infusion of galls; but when the mixture is exposed to the

"Ising lass is glue or gelatine nearly pure, as has been shown by Mr Hatchett.

+ Phil. Trans. 1803. p. 235. and 250.

Trommsdorf, Gehlen, iii. 144. § Ibid. alkalies,

Book II. Division II.

Of earths.

heat of boiling 'water, part of the ammonia flies off, a precipitate falls, consisting of most of the tannin and gallic acid, while the extract remains in solution §.

10. When barytes or lime water is poured into a solution of tannin, a precipitate falls, consisting of tannin combined with the earth, and the solution becomes nearly colourless. The precipitate dissolves with difficulty in water, and does not act upon the infusion of glue till the earth is saturated with an acid \*.

When newly precipitated magnesia is agitated with the infusion of tannin, it unites with a portion of it, and forms a smoky brown powder insoluble in water, but soluble in acids. Alumina produces the same effect, and forms a similar compound  $\dagger$ .

When barytes, strontian, or lime water, is poured into the infusion of galls, an olive coloured precipitate falls, which consists not only of the tannin, but also of the extract, and most of the gallic acid combined with the earth. When magnesia is mixed or boiled with this infusion, it combines with all its constituents; the gallate remains mostly in solution, and gives the liquid a green colour; while the tannin and the extract form with the magnesia an insoluble compound, and give it a dirty yellow colour. Alumina in small quantity produces exactly the same effect; but when used in a greater proportion, it separates all the constituents of the infusion ‡.

When the earthy carbonates are boiled in the infusion of galls, they separate the tannin and the extract, while

- § Davy, Phil. Trans. 1803, p. 241.
- \* Trommsdorf, Gehlen' Jour. iii. 145.
- ‡ Davy, Phil. Trans. 1803, p. 241.

+ Ibid.

they combine with the acid, and form with it a salt Chap. III. which remains in the liquid, and gives it a green colour\*.

11. Most of the acids have the property of combining with tannin, and of forming solutions more or less soluble. Acetic, phosphoric, oxalic, and malic acids, occasion no precipitate when dropt into a concentrated solution of nutgalls. Arsenic acid produces a copious precipitate, soluble in boiling water, and precipitating glue after the acid has been neutralized by an alkali. Muriatic acid likewise produces a precipitate mostly soluble in hot water. The same remark applies to sulphuric acid. But this acid alters and gradually decomposes tannin. Nitric acid produces no precipitate in the infusion of nutgalls. The mixture becomes hot, and assumes a red colour, which gradually changes to a yellow. By the action of this acid a bittertasted substance is formed, which possesses the properties of malic acid t.

12. When tannin is distilled, it yields an acid liquor, which blackens solutions of iron, because it contains a little tannin unaltered ; there comes over also some empyreumatic oil, and a voluminous coal remains behind, amounting to  $\frac{1}{10}$  of the tannin distilled  $\ddagger$ .

13. Such are the properties of the tannin of nutgalls, as far as they have been ascertained. The difficulty of procuring it in a state of purity renders some of them

- \* Davy, Phil. Trans 1803, p. 241.
- † Trommsdorf, Gehlen's Jour. iii. 142.
- \$ Proust, Ann. de Chim. XXXV. 35-

Of acids.

Book II. Division II.

Writing ink. ambiguous, and has induced chemists to employ as reagent the entire solution of nutgalls.

This solution is employed in considerable quantities by the dyers, and it forms the principal ingredient in writing ink. It is not known at what period this important liquid came into use; but the ink of the ancients was composed of very different ingredients, being analogous to the ink used by the printers at present. We are indebted to Dr Lewis for a valuable set of experiments on the best mode of making ink.

This liquid consists of a solution of sulphate of iron in the infusion of nutgalls, and seems to owe its black colour chiefly to a combination of the tannin with the oxide of iron, or perhaps with the sulphate, and partly also to the combination of gallic acid and oxide of iron. The fullest black is produced when equal weights of green vitriol and galls are used ; but the ink very soon fades. To make it permanent, the galls ought to be thrice the weight of the vitriol. No other solution of iron but the sulphate forms with nutgalls a full black. When the mixture of the infusion of nutgalls and green vitriol is diluted with much water, the black matter precipitates, and forms a sediment not again soluble. The addition of logwood increases the blackness of the The following formula was ascertained by Dr ink. Lewis to yield the best ink. mariar as draw have is

> Logwood......1 ounce Nutgalls in powder....3 Green vitriol ......1

Water ..... 1 to 2 quarts

Boil the logwood and nutgalls in the water, adding new liquid in proportion to the evaporation, then strain through a cloth, and add the vitriol to the water, add-

## TANNIN.

ing at the same time from one to two ounces of gum Chap. III. arabic. As soon as these have dissolved, the ink is fit for use\*. Some recommend the addition of a little cloves in powder to prevent mouldiness.

14. Mr Proust has announced it as his opinion, that there exist various species of tannin in the vegetable kingdom, differing from each other like the oils, resins, &c. He has even enumerated several of these varieties, and pointed out their characteristics +.

It is by no means unlikely that this opinion is well Species of founded, and the experiments of Mr Hatchett serve to confirm it : But it is impossible to admit it as demonstrated till a process be discovered for obtaining tannin in a state of purity; for the differences between the varieties pointed out by Proust may be owing to the presence of foreign substances which disguise its properties. At any rate, this subject will come under our consideration more properly in the Second Part of this Work, when we enumerate the different vegetable substances that contain tannin.

# II. ARTIFICIAL TANNIN. oten? ell .stin

THE important discovery, that a substance possessing Discovery. similar properties to the tannin of nutgalls may be formed artificially by a very simple process, was made by Mr Hatchett in the course of a set of experiments on the slow carbonization of vegetable bodies, and detailed by him in two papers read to the Royal Society in 1805.

\* See Lewis's Phil. Com. p. 377. Ann. de Chim xlii. 94

tannin.

Book II. Division II. Formation.

1. To form this artificial tannin, we have only to digest diluted nitric acid on charcoal till the whole, or nearly the whole, is dissolved. Mr Hatchett usually employed 100 grains of charcoal, and 500 grains of nitric acid of the specific gravity 1.40, diluted with twice its weight of water. On heating this mixture in an open matrass a considerable effervescence was produced, and much nitrous gas escaped. After two days digestion, more nitric acid was added, and the digestion was continued till the solution was complete. The solution thus obtained was transparent, and of a dark brown colour ; which being evaporated to dryness, leaves a brown coloured mass. This is the artificial tannin. To free it from the last portions of nitric acid, Mr Hatchett found the best method was to dissolve it repeatedly in water, and evaporate cautiously to dryness with a gentle heat.

By this method 100 grains of charcoal were converted into 120 grains of *artificial tannin*; but of these Mr Hatchett supposes three grains to be moisture.

Properties.

2. Tannin thus prepared is a substance of a brown colour, has considerable lustre, and breaks with a vitreous fracture. Its taste is bitter and highly astringent. It has no smell.

It dissolves readily in cold water, forming a transparent solution of a deep brown colour. Alcohol also dissolves it\*.

\* The alcohol used by Mr Hatchett was probably weak. The action of pure alcohol has not been tried. Were it soluble in it, this would form a marked distinction between natural and artificial tannin. I tried the effect of alcohol of she specific gravity 0.800, the strongest I had in my possession. It formed a pale yellow solution.

## TANNIN.

3. The solution of artificial tannin immediately precipitates glue, or isinglass, from water. The precipitates are more or less brown according to the strength of the solutions, and always insoluble both in bot and cold water. To ascertain the proportion in which these bodies unite, Mr Hatchett dissolved 50 grains of artificial tannin in 4 oz. of water, and then precipitated by means of a solution of isinglass. Forty-six grains of the tannin were precipitated in combination with eightyone grains of isinglass. Hence the precipitate is composed of about

> 36 tannin 64 isinglass

#### 100

The solution containing the four grains not precipitated by the isinglass being evaporated to dryness, left a light brittle substance of a pale brown colour, smelling strongly of prepared oak bark, especially when dissolved in water. The solution tasted bitter, and from its properties approached nearer to the vegetable matter called *extractive* than *tannin*; a proof that even the artificial tannin prepared from charcoal is not quite free from foreign bodies.

4. When sulphuric acid is added to a solution of aracids. tificial tannin, a copious brown precipitate falls, soluble in boiling water, and capable of throwing down gelatine. Muriatic acid produces precisely the same effect. Artificial tannin dissolves readily in nitric acid, but is not altered in its properties, though that acid be repeatedly distilled off it. In this respect it differs very materially from all the species of natural tannin hitherto examined, which were found by Mr Hatchett to be en-

Vol. II.

Action of acids.

Chap. III. Precipitates glue. Book II. Division II.

Alkalies.

tirely decomposed by nitric acid, though with different degrees of facility.

5. Artificial tannin unites readily with the alkalies, both fixed and volatile. When dissolved in ammonia, evaporated to dryness, and again dissolved in water, the new solution does not precipitate gelatine unless it be previously mixed with a small portion of muriatic acid. A proof that it still retains the ammonia in combination. When the fixed alkalies are added to a solution of artificial tannin, the colour is immediately deepened, and after some hours the solution becomes turbid. Carbonate of potash produces the same effect, and after some time a brown magma is deposited.

Earths,

Oxides,

6. The alkaline earths unite with artificial tannin, and form compounds little soluble in water. Hence it forms a precipitate when mixed with nitrates of lime, barytes, &c.

7. It precipitates likewise most of the metallic oxides from their solutions in acids. The colour of the precipitate is usually brown, inclining to chocolate.

Action of heat. 8. When artificial tannin is thrown upon a hot iron, it emits an odour similar to that of burning feathers. When exposed to a graduated heat in a retort, there passes over, in the first place, a portion of water; and this is succeeded by a little nitric acid, from which it is difficult to free it completely. A little yellow liquor next makes its appearance; and upon raising the fire, ammoniacal gas is disengaged with great rapidity. This is followed by the evolution of carbonic acid gas, together with a small portion of gas, which seems to possess the properties of azote. A bulky coal remains in the retort, amounting in weight to 0.425 of the original tannin. This coal being burned, left some brown ashes, Chap. III. consisting chiefly of lime.

From this decomposition by the action of fire, it is Constituobvious, that artificial tannin is composed of oxygen, azote, hydrogen, and carbon. The last ingredient obviously predominates; though the proportions have not hitherto been ascertained.

Such are the properties of the artificial tannin from charcoal, as far as they have been hitherto ascertained. by Mr Hatchett, to whom we are indebted for all the facts above detailed. From the experiments of this indefatigable chemist, we learn that every kind of charcoal yields it equally, from whatever substance it has been formed, whether vegetable, animal, or mineral, provided it be in the state of charcoal. But the action of nitric acid on charcoal, though the readiest and easiest process, and that which yields the greatest quantity, is not the only one by means of which artificial tannin may be formed. Mr Hatchett has pointed out two others, by means of which certain vegetable substances may be converted into tannin.

9. The first of these consists in digesting nitric acid Second vawith certain substances that appear to contain an un- tificial tan-1 common portion of carbon in their composition; indigo, for instance, and many of the bodies called resins. Indigo dissolves readily in diluted nitric acid, and the solution, when gently evaporated to dryness, leaves an orange-coloured mass of an intensely bitter taste, soluble in water, and possessing the property of forming an insoluble precipitate with gelatine. Hence it resembles tannin; but it acts more feebly on the metallic salts than tannin from charcoal. A similar substance was procured from common resin by digesting it for a long . Cc2

ents.

ricty of arnin

Book II. Division II.

Third variety. time in diluted nitric acid. Most of the resins and gum resins gave a similar product; but no tannin could be procured from the gums.

10. The other process for procuring artificial tannin consists in dissolving resins and camphor in sulphuric acid. digesting the solution till it becomes black, and then precipitating by throwing it into cold water. A black powder falls. If this powder be digested in alcohol, a brown substance is taken up, which is soluble both in water and alcohol, forms an insoluble precipitate with gelatine, but acts only feebly on oxy-sulphate of iron. Camphor by this process yields nearly half its weight of a brown resinous-like matter, which possesses the property of forming an insoluble precipitate with gelatine; and when digested with a little nitric acid, becomes precisely similar to tannin from charcoal.

Thus there are three species of artificial tannin. 1. Tannin procured by the action of nitric acid on charcoal. 2. Tannin, by digesting nitric acid on indigo and resins. 3. Tannin, by dissolving resins or camphor in sulphuric acid \*.

Such are the properties of the colorific acids. They act with most energy on metallic solutions, forming precipitates which vary in colour according to the metal. It is this property which renders them of so much importance in a chemical point of view. The colour of the precipitates which each of these bodies forms with the different metallic bodies, as far as is known at present, may be seen from the following **LABLE**.

\* See Mr Hatchett's papers, Phil. Trans. 1805 and 1806. From, which all the facts respecting artificial tannin have been taken.

Chemical uses of the colorific acids.

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Chap, III.

	per. Iron.	k 0. or sulphur	k Black	· Kall	en- Blue	wn Blue	nies Black	e Brown
	Copper.	Black	Black		Green- ish-yel.	Brown	0 Becomes olive	Olive
State and	Osmium.	0					Blue	
	Iridium.	Traile St			O Becomes colourless	all	0 Becomes colourless	
	Mercury. Palladium. Rhodium.	ANNA -	0	-	0		Careford Contraction	
	Palladium.	Dark brown	Black ?		Olive	ALC: NO.	Disci	Arright
	Mercury.	Black	Black Black?	0	White	- Orange yellow	Orange yellow	Yellow
	Silver.	Black	Black	White	White	Yel brown	Yei brown	Yellow Yellow
	Platinum.	Reduced	Black	0	.0	0	0	×
	Gold.	Reduced	Black	Reduced	Yell white	Reduced	Reduced	Reduced
		Sulphureted Reduced Reduced Black hydrogen.	Hydrosulph. Black of potash.	Prussic acid. Reduced	Prussiate of potash.	Gallic acid. Reduced	Infusion of Galls.	Tannin from Reduced Charcoal.

Book II. Division II.

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							al and a second
Manga- nese.	0	White		Yellow white	0	12	
Cobalt.	0	Black		Brown	0	Yellow white	
Arsenic.	Yellow	Yellow		White	0	0	Yellow?
Bismuth. Antimony Tellurium. Arsenic.		Brown Yellow Black		0		Yellow	
Antimony	Orange	Orange Brown.		0	White	White	Yellow
Bismuth.	Black	Black		White	Orange	Orange	1212 El 1
Zinc.	White	White		White	0	0	0
Lead.	Black	Black		White	White	White	Brown
Tin.	Brown	Black		White	0	Brown	Black grey
Nickel.	0	Black		Green	White	Grey	
	Sulphureted hydrogen.	Hydrosulph. Black of potash.	Prussic acid.	Prussiate of potash.	Gallic acid. White	Infusion of Galls.	Tannin from Charcoal.

# [TABLE continued.]

Cerium.	0 -	Brown		White	0	0	2
Niccola- num.	igia : 1	2.33	10-94	ause	e suc	22	a
Columbi- um.		Red cho- colate		Olive		Orange	
Titanium.	0	Bottle green	ino en roka i	Grass green		Reddish brown	adote-
Molybde- Urasium. Tungsten. Titanium.	tarda. 2 in N		n eda	Brown		Straw yellow	
Uranium.	Anife and	Brown yellow		Brown red		Choco- late	
	Choco- late	Reddish brown		ender Republic		escolo ponessi sidilitate	
Chromium.		Green		Green		Brown	
	Sulphureted hydrogen.	Hydrosulph. of Potash.	Prussicacid.	Prussiate of Potash.	Gallic acid.	Infusion of Galls.	Tannin from Charcoal.

TABLE continued.]

Chap. III.

### COMPOUND COMBUSTIBLES.

Book II. Division II.

## CHAP. IV.

## OF COMPOUND COMBUSTIBLES.

Number of th compound combusti- do bles. be

THE compound combustibles are almost all composed of carbon and hydrogen, or of carbon, hydrogen, and oxygen. They are a very numerous class of bodies, comprehending the greater number of animal and vegetable substances, and of the products obtained from these substances. But the present state of chemistry does not permit us to take the term in that comprehensive sense : The investigation of vegetable and animal bodies is too incomplete ; their properties are too imperfectly known to allow us to introduce them into the first principles of the science; and the utility of the greater number of them as chemical instruments is too inconsiderable to warrant any such introduction, even if their properties were completely investigated. For these reasons, it will be proper to treat in this Chapter of those compound combustibles only which are employed in chemistry as instruments of investigation, reserving the remainder for the Second Part of this Work. These may be reduced under five classes; namely,

1. Alcohol	4.	Fixed	oils

2. Ether

5. Bitumens

3. Volatile oils

The properties of these bodies form the subject of the following Sections.

#### ALCOHOL.

Chap. IV.

# SECT. I.

adi barti persia

# OF ALCOHOL.

THE liquid called alcohol, or spirit of wine, is obtained History, by distilling wine, beer, and similar fermented liquors. These liquors appear to have been known in the earliest ages. The Scripture informs us that Noah planted a vineyard and drank wine; and the heathen writers are unanimous in ascribing the invention of this liquor to their earliest kings and heroes. Beer, too, seems to have been discovered at a very remote period. It was in common use in Egypt during the time of Herodotus\*. Tacitus informs us that it was the drink of the Germans +. Whether the ancients had any method of procuring ardent spirits from these or any other liguors does not appear. The Greeks and Romans seem to have been ignorant of ardent spirits altogether, at least we can discover no traces of any such liquor in their writings : But among the northern nations of Europe, intoxicating liquors were in use from the earliest ages. Whether these liquors resembled the beer of the Germans we do not know.

At what period these liquors were first subjected to distillation is unknown; though it can scarcely have preceded the time of the alchymists. The process is simple. Nothing more is absolutely necessary than

> + De Morib. Germ. ch. xxiii. \* Lib. ii. n. 77.

Book II. Division II. to boil them in a still. The first portion of what comes over is ardent spirits. It is certain, at least, that the method of procuring ardent spirits by distillation was known in the dark ages; and it is more than probable that it was practised in the north of Europe much earlier. They are mentioned expressly by Thaddæus, Villanovanus, and Lully \*.

It is by the distillation of fermented liquors that ardent spirits are obtained; and they receive various names according to the nature of the substance employed. Thus brandy is procured from wine, rum from the fermented juice of the sugar cane, whisky and gin from the fermented infusion of malt or grain. Now ardent spirits, whatever be their name, consist almost entirely of three ingredients; namely, water, pure spirit or alcohol, and a little oil or resin, to which they owe their flavour and colour.

Rectified spirits. 1. When these spiritous liquors are redistilled, the first portion that comes over is a fine light transparent liquid, known in commerce by the name of *rectified spirits*, and commonly sold under the denomination of alcohol or spirit of wine. It is not, however, as strong as possible, still containing a considerable portion of water.

Preparation of alcohol. The method usually practised to get rid of this water is to mix the spirits with a quantity of very dry and warm salt of tartar  $\ddagger$ . This salt has a strong attraction for water, and the greatest part of it is insoluble in alcohol. It accordingly combines with the water of

\* Bergman, iv. art. ii. 4.

+ Impure potash not fully saturated with carbonic acid.

the spirit; and the solution thus formed sinks to the Chap. IV. bottom of the vessel, and the alcohol, which is lighter, swims over it, and may easily be decanted off; or, what is perhaps better, the solution of potash may be drawn off from below it by means of a stop-cock placed at the bottom of the vessel\*. The alcohol, thus obtained, contains a little pure potash dissolved, which may be separated by distilling it in a water bath with a very small heat. The spirit passes over, and leaves the potash behind. It is proper not to distil to dryness. This process is first mentioned by Lully. The liquid procured by means of it has been usually distinguished by the name of alcohol.

Alcohol is said to have been discovered, or at least first accurately described, by Arnold de Villa Nova, who was born about the end of the thirteenth century. This chemist, who was professor of medicine at Montpelier, first formed tinctures, and introduced them into medicine t.

The specific gravity of spirits, as highly rectified as Strength of possible by repeated distillations, seems to be about 0.820, at the temperature of 60°; but the alcohol of commerce, which is nothing else than rectified spirits, is seldom under .8371. By means of salt of tartar Muschenbroeck brought it as low as .815; but, in general, the alcohol concentrated by that process is not under .821, owing to the weakness of the spirits employed. Even at the specific gravity .815 the alcohol is by no

common alcohol.

\* See this process described by Hoffman as new, in his Observationes Phys.-Chym. Select. p. 36. published in 1722.

+ He has said also to have been the first who obtained the oil of turpentine. He procured it by distilling turpentine, and employed it as a polyent of resins.

#### COMPOUND COMBUSTIBLES.

Book II. Division II. means pure, still containing a considerable portion of water. Dr Black, by repeated distillations off muriate of lime, obtained it as low as .800; but it was Lowitz of Petersburgh who first hit upon a method of obtaining alcohol in a state of absolute purity, or at least very nearly so. His process was published in 1796\*; and the same year Richter made known another, by which the same purification was accomplished with still greater facility  $\ddagger$ .

Method of procuring pure alcohol.

The process of Lowitz is as follows: Take a quantity of fixed alkali ‡ perfectly dry, and still warm, and nearly fill with it a retort. Upon this pour such a quantity of alcohol (previously brought to .821 by means of salt of tartar) as can be absorbed by the alkali completely, so that the whole shall have the appearance of a solid mass without any alcohol swimming above. In general, the proportion ought to be two parts alkali and one part alcohol. Allow this mixture to remain for 24 hours, and then distil by a heat so moderate, that about two seconds elapse between the falling of the drops of alcohol from the beak of the receiver. When this interval increases, the receiver must be changed; for it is a sign that all the strong alcohol has come over. What comes over next is weaker. By this process Lowitz obtained alcohol of the specific gravity 0.791 at the temperature of 68°.

When Richter repeated the experiment of Lowitz, he reduced the alcohol to the specific gravity 0.792 at the temperature of 68°, but could not bring it any lower.

\* Crell's Annals, 1796, i. 195.

+ Ibid. ii. 211.

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‡ I presume in the state of sub-carbonate.

#### ALCOHOL.

He found, upon trial, that the following method, which is much more expeditious, answered equally well with that of Lowitz : He exposed a quantity of the salt called muriate of lime to a red heat, reduced it to powder, and introduced it while yet warm into a retort, and poured over it at intervals a quantity of alcohol, of 0.821, nearly equal to it in weight. A violent heat was produced. The retort was put upon a sand-bath, a receiver adjusted, and the liquid made to boil. The salt was dissolved, and formed with the alcohol a thick solution. The portion that had passed over into the receiver was now poured back, and the whole distilled by a gentle boiling nearly to dryness. The alcohol that came over was of the specific gravity 0.792 at the temperature of 68°.

2. Alcohol obtained by these processes is a transpa- Properties. rent liquor, colourless as water, of a pleasant smell, and a strong penetrating agreeable taste. When swallowed it produces intoxication. Its properties differ somewhat according to its strength. When procured by Lowitz's or Richter's process, we may distinguish it by the name of pure alcohol, as no method known can deprive it of any more water. When the specific gravity is higher, the alcohol is contaminated with water, and the proportion of that liquid present increases with the specific gravity. Chemists, in general, have employed this impure alcohol, or this mixture of alcohol and water, in their experiments; and as they have too often neglected to point out the specific gravity of the spirit used, we are still in some measure ignorant of the properties of this important liquid \*.

\* Fahrenheit was one of the first who ascertained some of the re-

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Action of heat and sold. 3. Alcohol is exceedingly fluid, and has never been frozen, though it has been exposed to a cold so great that the thermometer stood at  $-69^{\circ}$ . Indeed, Mr Walker sunk a spirit of wine thermometer to  $-91^{\circ}$ , without any appearance of congelation.

It is a very volatile liquid. Fahrenheit found that alcohol of the specific gravity of about  $\cdot 820$ , at the temperature of  $60^{\circ}$ , boiled when heated to  $176^{\circ *}$ . When of the specific gravity  $\cdot 300$  it boils at  $173\frac{1}{2}^{\circ}$ . At this heat it assumes the form of an elastic fluid, capable of resisting the pressure of the atmosphere, but which condenses again into alcohol when that temperature is reduced. In a vacuum it boils at  $56^{\circ}$ , and exhibits the same phenomena: so that were it not for the pressure of the atmosphere, alcohol would always exist in the form of an elastic fluid, as transparent and invisible as common air. This subject was first examined with attention by Mr Lavoisier  $\ddagger$ . The fact, however, had been known long before.

Combination with water. 4. Alcohol has a strong affinity for water, and is miscible with it in every proportion. The specific gravity varies according to the proportion of the two li-

markable properties of alcohol with exactness. His alcohol was of the specific gravity 825 at the temperature of 48°. See *Pbil. Trans.* 1724. vol. xxxiii. p. 114. Fourcroy informs us that the specific gravity of the most highly rectified alcohol is 0.8293, without specifying the temperature. The extremity of Baumé's hydrometer for spirits (according to Nicholson's table, *Quarto Jour.* i. 39.) answers to the specific gravity 817, temp. 55°. This may be considered as beyond the strength of the alcohol used. In Germany, before Lowitz's experiments, the strongest alcohol seems seldont to have exceeded 0.821 at 68°; and in this country it is commonly considerably weaker. The highest point of Clark's hydrometer corresponds with alcohol of about .834 at 30°. Dr Lewis states the purest alcohol of the specific gravity .820-Neuman's Chem.

\* Phil. Trans. 1724. vol. XXXIII. p. I. + Jour. de Phys. 1785.

quids combined; but, as happens in almost all combinations, the specific gravity is always greater than the mean of the two liquids; consequently there is a mutual penetration : and as this penetration or condensation varies also with the proportions, it is evident that the specific gravity of different mixtures of alcohol and water can only be ascertained by experiment. As the spiritous liquors of commerce are merely mixtures of alcohol and water in different proportions, and as their strength can only be ascertained with precision by means of their specific gravity, it becomes a point of very great importance to determine with precision the proportion of alcohol contained in a spirit of a given specific gravity : and as the specific gravity varies with the temperature it is necessary to make an allowance for that likewise.

The importance of knowing with precision the proportion of alcohol contained in spirits of every specific gravity, has induced many different persons to make experiments in order to ascertain this point with exactness; but as they set out from alcohol of very different strengths, it is not easy to compare their results with each other. We have seen that the pure alcohol, by Lowitz's process, is of the specific gravity .791 at the temperature of 65°. That chemist mixed various proportions of this alcohol with given weights of pure water, and after allowing the mixtures to remain for 24 hours, took the specific gravity of each at the temperature of 68°. The following Table exhibits the result of these experiments. The first two columns contain the proportion of alcohol and water (in weight) mixed together, and the third the specific gravity of the mixture at 68°. I have added a fourth column, containing

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## COMPOUND COMBUSTIBLES.

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the specific gravity at 60°, the temperature commonly preferred in this country \*. blunkonse the specific s

Table of the strength of alcohol of various densities.

100 ]	Parts.	Sp. Gi	avity.	100 Parts.		Sp. Gr	11.31	
Alcoh.	Wat.	at 68°.	at 60°.	Alcoh.	Wat.	at 68°.	at 60°.	inte
100		791	796	70	30	868	871	ngd1
99	1	794	798	69	31	870	874	there
98	2	797	801	68	32	872	875	ditt
97	3	800	804	67	33	875	879	ofia
96	4	803	807	66	34	877	880	
95	5	805	809	65	35	880	883	
94	6	808	812	64	36	882	886	99237
93	7	811	815	63	37	885	889	Tax
92	8	813	817	62	38	887	891	ntes
91	9	816	820	61	39	889	893	10.150
90	10	815	822	60	40	892	896	
89	11	821	825	59	41	894	898	(hite
88	12	823	827	58	42	896	900	267
87	13	826	830	57	43	899	903	£ ···
86	14	828	832	56	44	901	904	more
85	15	831	835	55	45	903	906	1000
84	16	834	838	54	46	905	908	urañ.
83	17	836	840	53	47	907	910	qua
82	18	839	843	52	48	909	912	new.
81	19	842	846	51	49	912	915	Seres.
80	20	844	848	50	50	914	917	
79	21	847	851	49	51	917	920	
78	22	849	853	48	52	919	922	20.1
77	23	851	855	47	53	921	924	pal
76	24	853	857	46	54	923	926	100
75	25	856	860	45	55	925	928	- all
74	26	859	863	44	56	927	930 -	
73	27	861	865	43	57	930	933	There's
72	28	863	867	42	58	932	935	的时
71	29	866	870	41	59	934	937	1 30

\* Crell's Annals, 1796, i. 202.

ALCOHOL.

100 Parts.		Sp. Gi	ravity.	100	Parts.	Sp. Gravity.	
Alcoh.	Wat.	at 68°.	at 60°.	Alcoh.	Wat.	at 68°.	at 60°.
40	60	936	939	19	81	974	975
39	61	938	941	18	82	976	7 JL
38	62	940	943	17	83	977	
37	63 -	942	945	16	84	978	21/122
36	64	944	947	15	85	980	
35	65	946	949	14	86	981	
34	66	948	951	13	87	983	
33	67	950	953	12	88	985	
32	68	952	955	11	89	986	
31	69	954	957	10	90	987	
30	70	956	958	9	91	988	
29	71	957	960	8	92	989	
28	72	959	962	7	93	991	Res Office
27	73	961	963	6	94	992	
26	74	963	965	5	95	994	
25	75	965	967	4	96	995	
24	76	966	968	3	97	997	
23	77	968	970	2	98	998	
22	78	970	972	1	99	999	and the
21	79	971	973		100	1000	
20	80	973	974	1	23.01		

The importance of this object, both for the purposes of revenue and commerce, induced the British Government to employ Sir Charles Blagden to institute a very minute and accurate series of experiments. An account of these was published by Blagden in the Philosophical Transactions for 1790; and a set of Tables, exhibiting the result of them, was drawn up by Mr Gilpin, who had performed the experiments, and published in the Philosophical Transactions for 1794. The following Table, extracted from these, contains the specific gravity of different mixtures of alcohol and water at *Vol. II*. D d

Gilpin's tables.

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Book II. Division II. every 5° of temperature from  $30^{\circ}$  to  $100^{\circ}$ . The alcohol employed as a standard was of the specific gravity 0.825 at the temperature of  $60^{\circ}$ ; and was composed, according to the experiments of Mr Gilpin, of 100 parts of alcohol of the specific gravity 0.814 and 4.5 of water. From the preceding Table, we see that alcohol of .825 is composed of .89 pure alcohol

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ng Table, extracted for three, contains the solid to a start of the solid to the so

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Real Specific Gravities at the different Temperatures.

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100 alcohol 95 water.	16686.	06756	93592	03382	17118	92963	92758	92546	92333	9.2111	16816	6716	91511	91290	91066
roo alcoholl roo alcoholl roo alcoholl roo alcohol roo	14780.	93541	9334I	93131	61676	92707	92499	92283	92069	91849	91622	91465	91248	91029	90805
100 alcohol 85 water.	•93474	93274	93072	92859	92647	92436	92225	92010	91793	01569	91340	91186	1 9606	74709	90522
roo alcohol 85 water.	.93191	92986	92783	92570	92358	92145	91933	91715	91493	91270	91016	90882	90906	90443	90215
100 alcohol 75 water.	-92889	92380	92476	92264	92051	91837	91622	91400	91181	90952	90723	90558	90342	90119	89889
100 alcohol 70 water.	.92563	92355	92151	91937	91723	91502	91287	91060	74806	11006	90385	90209	89088	89763	89536
too alcohol 65 water,	71220.	92009	91799	+8010	01370	91144	90927	20206	90434	90252	90021	89843	89617	89390	89158
teo alcohol 60 water.	.91847	91640	91428	91211	26006	90768	90549	90328	10106	89872	89639	89460	89230	89003	- 88769
coo alcohol roo alcohol 50 water. 55 water.	.91449	91241	91026	90812	90596	19806	90144	89920	89695	89464	89225	89043	88817	88588	88357
roo alcohol 50 water.	.91023	90811	90596	90380	00100	89933	10168	89479	89252	89018	88731	88605	-88376	88146	37915
Heat.	300	35	40	45	50	55	60	65	02	75	80	85	06	.95.	100

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Real Specific Gravities at the different Temperatures.

Real Specific Gravities at the different Temperatures.

Heat.	100 alcohol 100 water.	100 alechol 95 alechol 90 alechol 86 alechol 80 alechol 75 alechol 70 alechol 100 water. 100 water, 100 water. 100 water.	90 alcehol	85 alcohol	80 alcohel 100 water.	75 alcohol 100 water.	70 alcohol 100 water.	100 alc hol go alcohol go alc hol 88 alcohol 80 alcohol 75 alcohol 70 alcohol 65 alcohol 60 alc hol 100 water. 100 water, 100 water. 100 water. 100 water. 100 water.	60 alcohol 100 water.	55 alcohel IOO water.
300	.94222	·94447	<sup>2</sup> 94675	07616,	82150.	95429	18926.	.95944	.96209	.96470
35	94025	94249	94484	94734	94988	95246	92502	95772	96048	96315
40	93827	94058	94295	94547	94802	95060	95328	95602	95879	96159
45	93621	93860	94096	94348	94005	17840	95143	95423	95705	95993
50	93419	93658	93897	94149	94414	94683	94958	95243	95534	95831
55	93208	93452	93696	93948	94213	94486	94767	95057	95357	95662
60	93002	93247	93493	93749	94018	94296	94579	64876	95181	95493
65	92794	93040	93285	93546	93822	94099	94388	94689	95000	95318
10	92580	92828	93076	93337	93616	93898	94193	94500	94813	95139
75	92364	92613	92865	93132	93413	93695	93989	94301	94623	94957
80	92142	92393	92646	92917	93201	93488	93785	94102	94431	94768
85	91969	tes philits a	CONTRACT	Distances of	and a start	「「日本」」	- ON IN STOL	100000	Survey Brin	and the second
06	91751	Or Shain 25	Station is	a standard the	の一日の	「日本の	and a line	H-CHARTER	Introde a	Station of
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ALCOHOL.

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Book II. Division II.

#### COMPOUND COMBUSTIBLES.

Real Specific Gravities at the different Temperatures.

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By the excise laws at present existing in this coun- Chap. IV. try, the duty on spirits is levied by the bulk, estimated at a particular strength, to which all spirits of whatever, strength are brought by means of a set of tables calculated. This strength is regulated by a very inconvenient hydrometer, invented in 1730 by Mr Clarke\*, since which time it has undergone various changes and improvements. This instrument was adapted to a very absurd kind of language, which had previously come intocommon use among dealers, and seems from them tohave made its way into the excise laws. A mixture of equal bulks of alcohol and water was called proof spirit, and sometimes double spirit. Clarke's hydrometer, consists of a thin copper ball, terminating above in a flat, slender stem, and below, in a metallic button, to keep it perpendicular. It is so light as to swim in pure alcohol. There is a mark upon the middle of the stem; and small weights accompany the instrument, to be put on in order to suit the various temperatures of the liquid. There is a weight marked proof, so adjusted that when it is placed upon the stem along with the proper weight for the temperature, the stem sinks till the mark on the middle of it is on a level with the surface of the liquid.

From an act of parliament passed in 1762, we learn that, at the temperature of 60°, the specific gravity of proof spirit ought to be 0.916. But Clarke's hydrometer, loaded with the proper weights, sinks to the mark indicating proof in spirits of the specific gravity 0.920, at the same temperature. From the table of

\* See the first description of it in Phil. Trans. 1730, vol. xxxvi. p. 277.

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to proof, it is said

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## COMPOUND COMBUSTIBLES.

Book II. Division II. Lowitz, given above, we learn that a mixture of equal weights of water and pure alcohol has the specific gravity '917 at 60°. The legal proof spirit differs but little from this; Clarke's proof consists of 49 parts of pure alcohol and 51 of water. The near coincidence of these numbers to the truth, indicates a considerable approach to accuracy. Had Sir Charles Blagden made choice of an alcohol of '800 for his standard, the specific gravity of proof spirit would have been found to deviate very little from that of Clarke. But if by proof spirit were to be understood equal *bulks* of water and alcohol, as was doubtless the case, then both the legal and Clarke's proof differ very far from the truth.

The strength of spirits stronger than proof, or overproof, as it is termed, is indicated on Clarke's hydrometer by the bulk of water necessary to reduce a given bulk of spirits to the specific gravity denominated proof. Thus, if one gallon of water be required to bring 20 gallons of the spirits to proof, it is said to be one to 20 over proof; if one gallon of water be necessary to bring 15, 10, 5, or 2 gallons of the spirits to proof, it is said to be one to 15, one to 10, one to 5, one to 2 respectively, over proof, and so on.

The strength of spirits weaker than proof, or under proof, is estimated by the quantity of water which it would be necessary to abstract, in order to bring the spirits in question up to proof. Thus, if from 20 gallons of the spirits one gallon of water must be abstracted to bring it to proof, it is said to be one in 20 under proof; if from 15, 10, 5, 2, &cc. gallons of the spirits, one gallon of water must be abstracted to bring it to proof, it is said to be respectively one in 15, one in 10, one in 5, one in 2, &cc. under proof.

## ALCOHOL.

The following Table points out the specific gravity Chap. IV. of spirits of the various strengths indicated by Clarke's hydrometer at the temperature of 60° \*.

Degrees.	Sp. gravity.
1 in 2	9644
1 - 3	9543*
1 - 4	9458
1 - 5	9424
1 - 6	
1 - 7	9364
1 - 8	9344
1 - 9	
1-10	9320
1-15	9280
1-20	9265
Proof	9200
1 to 20	9162
1-15	
1-10	
1 - 9	
1 - 8	
	9047
1 - 6	
1 5	
ALL CHAILED IN PROPERTY OF	
Alcohol	
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Degrees of Clarke'shydrometer,

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To remove all confusion from the duties on spirits, they ought to be levied by the weight, and not by the bulk. This might be done with sufficient accuracy

\*Wilson's Tables, p. s .

## COMPOUND COMBUSTI BLES.

Book II. Division IL either by actual weighing, or by constructing tables indicating the weight from the bulk and specific gravity.

Action of air and oxygen on alcohol.

5. Neither common air nor oxygen gas has any action on alcohol in moderate temperatures, whether in the liquid or gaseous state; but in high temperatures the case is different. When set on fire in the open air it burns all away with a blue flame, without leaving any residuum. Boerhaaye observed, that when the vapour which escapes during this combustion is collected in proper vessels, it is found to consist of nothing but water. Junker had made the same remark : and Dr Black suspected from his own observations, that the quantity of water obtained, if properly collected, exceeded the weight of the alcohol consumed. This observation was confirmed by Lavoisier; who found that the water produced during the combustion of alcohol exceeded the alcohol consumed by about 1th part \*. Mr Saussure junior has shown that 100 parts of alcohol when burnt, yield 132 parts of water +. A proof that it contains a considerable proportion of hydrogen as a constituent.

When the vapour of alcohol is mixed with oxygen gas in the proper proportion, the mixture detonates when presented to a lighted taper, or when fired by electricity, as a mixture of oxygen and hydrogen gases do. This fact seems to have been first observed by Dr Ingenhousz, or at least his experiments on ether appear to have led to it ‡. The density of the vapour

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<sup>\*</sup> Mem. Par. 1781, p. 493.

<sup>+</sup> Nicholson's Journal, xxi. 263.

<sup>¿</sup> See his Experiences et Observations sur divers Objets de Phys. p. 173.

## ALCOHOL.

of alcohol is considerable, and hence the quantity of oxygen necessary to consume it is great. The products of the combustion are water and carbonic acid \*. 6, Alcohol has but little action on the simple combustibles. On hydrogen, carbon, and charcoal, it does not appear to have any effect.

It dissolves a little phosphorus when assisted by heat. This phosphorized alcohol exhales the odour of phosphureted hydrogen gas. When a little of it is dropt into a glass of water, a flame instantly makes its appearance, and waves beautifully on the surface of the water +. This phenomenon, which is occasioned by the emission of a little phosphureted hydrogen gas, can only be observed when the experiment is performed in a dark room. melers to da ... mode antenno boniren

When sulphur and alcohol are brought into contact Sulphuretin the state of vapour, they combine and form a reddish coloured liquid, which exhales the odour of sulphureted hydrogen. This compound was first formed by the Count de Lauraguais, who employed the following process. Some flowers of sulphur were put into a large glass cucurbite, having a glass vessel in its centre containing alcohol. A head was adjusted, the cucurbite placed in a sand-bath, and heat applied. The sulphur was volatilized, and the acohol converted into vapour at ouce. These meeting together in the head, united and formed the red liquor wanted ‡. It was supposed by

+ Brugnatelli, Ann. de Chim. xxiv. 71. This experiment was first made by Boyle. See Shaw's Boyle, iii. 196. \$ Mam. Par. 1758, p. 9.

Phosphureted alcohol

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<sup>\*</sup> Cruikshanks, Nicholson's Quarto Jour. v. 205.

Book II. Div on II. chemists that sulphur cannot be dissolved in alcohol, except by a similar process \*; but from the late experiments of Favre, this does not appear to be the case +. He digested, during 12 hours, one part of flowers of sulphur in eight parts of alcohol, of the specific gravity 0.837, in a heat not sufficient to produce boiling. The alcohol assumed a yellow colour, and acquired the smell and taste of sulphureted hydrogen. Another portion of the same alcohol was digested for a month, cold, on sulphur. The effect was the same. On trying alcohol of various strengths from .S17 to .867, he found, that the alcohol acted with more energy in proportion to its strength.

The sulphureted alcohol prepared by Lauraguais' method, contains about  $\frac{1}{50}$  th of sulphur. The sulphur is precipitated by water.

Action on alkalics, 7. Alcohol dissolves the fixed alkalies very readily, and forms with them a reddish-coloured acrid solution. It is from this solution only that these alkalies can be obtained in a state of purity. When heat is applied to it the alcohol may be distilled over. It appears however, to be partly decomposed; but the nature of the products has not been accurately ascertained. Ammonia also combines with alcohol with the assistance of heat : but at a temperature somewhat below the boiling point of alcohol, the ammonia flies off in the state of gas, carrying with it, however, a little alcohol in solution.

Earths,

8. None of the earths are acted upon by alcohol, un-

\* See the Elemens de Chymie of the Dijon Academy, iii. 287. Fourcroy's Connoissances Chymiques, viii. † Gehlen's Jour. ii. 343.

# ALCOHOL.

ess strontian and barytes be excepted. It absorbs about its own weight of nitrous gas, which cannot afterwards be expelled by heat ‡.

9. Of the acids, the sulphuric, nitric, and oxymuri- Acids, atic, decompose alcohol ; but all the other acids are souble in it, except the metallic acids, phosphoric acid, and perhaps also prussic acid.

10. Alcohol is capable of dissolving a great many Salts. saline bodies. A considerable number of these, with he quantities soluble, is exhibited in the following Tables\*.

Names of the Substances,	Tempera- ture.	240 parts of Al cohol dissolve
Oxysulphate of iron	potasti	Rinuste of
Nitrate of cobalt +	54.2°	240 parts
copper †	-54.5	240
alumina †	54.5	240
lime ‡	( 8 has	300
magnesia †	180.5	694
Muriate of zinc +	54.5	240
alumina †	54.5	240
magnesia †	180.5	1313
iron †	180.5	240
coppert		240
Acetate of lead +	154.5	240
copper §		1 Finite
Nitrate of zinc decomposed	thoritime.	Sulparts de
iron decomposed		
bismuth decomp	osed +	

# I. Substances dissolved in large Quantities ..

\$ Priestley, i. 379.

# Morveau, Jour. de Pbys. 1785.

Withering, Phil. Trans. Izzii. 336.

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## COMPOUND COMBUSTIBLES.

Book II. Division II. II. Substances dissolved in small Quantities.

STRUCTURE COULD AND BUILDING IN	240 parts of Alcohol
Names of the Substances.	at the boiling tempera-
te salpharie, titrie, antenymu	ture dissolve
Muriate of lime +	240 parts
Nitrate of ammonia +	214
Oxymuriate of mercury	
Succinic acid +	110. Ale 77.
Acetate of soda +	112
Nitrate of silver +	100
Refined sugar +	dulor 59 inninp bi
Boracic acid +	48 . 2010
Nitrate of soda +	23
Acetate of copper +	182.1
Muriate of ammonia +	17
Superarseniate of potash +	9
Oxalate of potash +	lad out to president of the Sal
Nitrate of potash †	
Muriate of potash +	1 Oxysnictate of 1
Arseniate of soda +	Andreale & cobrit
White oxide of arsenic +	8 60000
Tartrate of potash +	timula 1 . Com
Nitrate of lead §	i amit manne i
Carbonate of ammonia §	Sugar ( Bagene

III. Substances insoluble in Alcohol.

Muriate of zine

Sugar of milk	Sulphate of potash +
Borax †	soda +
Tartar †	magnesia+
Alum †	Sulphite of soda
Sulphate of ammonia †	Tartrate of soda and
lime †	potash
barytes §	Nitrate of mercury †
iron †	Muriate of lead +
copper †	silver ‡
silver †	Common salt +
mercury †	Carbonate of potash
zinc †	soda

These experiments were made chiefly by Macquer and Wenzel\*. The alcohol employed by Macquer was of the specific gravity 0.840. Wenzel does not give the density of his alcohol; but as he compares it with that of Macquer, we may suppose it nearly of the same strength. As the solubility of salts depends upon the strength of the alcohol employed, the experiments of these chemists must be considered as defective, because they have confined themselves to one particular density. This defect is in part supplied by the following very valuable Table of Mr Kirwan's, constructed from his own experiments †.

\* Verwandtschaft, p. 300. The solubility of all the salts marked  $\ddagger$  was ascertained by Wenzel; those marked  $\ddagger$ , by Macquer; and those marked  $\oiint$ , by Withering.

When alcabel containing certain antine bestire in as

Indior is set on the style fame is of encinged of different colours accerting tracht hody of the contract of scanting inges it yours by the accention and and contracts in the it press marks to of these stores of send contracts and

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Mundate of burytes It.

Muriare of magnic 21.2

+ On Mineral Waters, p. 274.

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Den Hannet

Book II. Division II.

; Solubility of Salts in 100 parts of Alcohol of different Densities.

			1.1.1.1		and an		
Salts.	Alcohol of						
naga tarat na sepad Tanta tarat ang an	0.900	0.872	0.848	0.834	0.817		
Sulphate of soda	0.	0.0	0.0	0.0.0	0.		
Sulph. of magnesia	1.	1.	0.	0.	0.		
Nitrate of potash	2.76	1. 14	l lo a	0.	0		
Nitrate of soda	10.5	6.	1.00	0.38	0.		
Muriate of potash	4.62	1.66	. 10 [17]	0.38	0.		
Muriate of soda	5.8	3.67	y Wenc	0.2	tas docut		
Muriate of ammon.	6.5	4.75	Calegos I	1.2	1 62 1		
Muriate of magne- sia dried at 120°	21.25		23.75	36.25	50.		
Muriate of barytes Ditto crystallized	1. 1.56			0·185 0·32	0.09		
Acetate of lime	2.4		4.12	4.75	4.88		

Its flame tinged by salts. When alcohol containing certain saline bodies in solution is set on fire, its flame is often tinged of different colours according to the body. Thus nitrate of strontian tinges it purple; boracic acid and cupreous salts tinge it green; muriate of lime gives it a red colour; nitre and oxymuriate of mercury a yellow colour.

# ALCOHOL.

11. Different opinions were entertained by chemists about the nature of alcohol. Stahl thought that it was composed of a very light oil, united by means of an acid to a quantity of water. According to Junker, it was composed of phlogiston, combined with water by means of an acid. Cartheuser, on the other hand, affirmed that it contained no acid, and that it was nothing else than pure phlogiston and water. But these hypotheses were mere assertions supported by no proof whatever. Lavoisier was the first who attempted to analyse it.

He set fire to a quantity of alcohol in close vessels by means of the following apparatus: BCDE (fig. 13.) is a vessel of marble filled with mercury. A is a strong glass vessel placed over it, filled with common air, and capable of containing about 15 pints (French). Into this vessel is put the lamp R filled with alcohol, the weight of which has been exactly determined. On the wick of the lamp is put a small particle of phosphorus. The mercury is drawn up by suction to the height IH. This glass communicates by means of the pipe LK with another glass vessel S filled with oxygen gas, and placed over a vessel of water T. This communication may be shut up at pleasure by means of the stop-cock M:

Things being thus disposed, a crooked red hot iron wire is thrust up through the mercury, and made to touch the phosphorus. This instantly kindles the wick, and the alcohol burns. As soon as the flame begins to grow dim, the stop-cock is turned, and a communication opened between the vessels S and A; a quantity of oxygen gas rushes in, and restores the brightness of the flame. By repeating this occasionally, the alcohol may be kept burning for some time. It goes out, how-Vol. II. E e

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tion.

#### COMPOUND COMBUSTIBLES.

Book II. Division II. gas.

> The result of this experiment, which Mr Lavoisier repeated a great number of times, was as follows :

Oxygen gas consumed ..... 90:5060

# Total.....167.2143

After the combustion, there was found in the glass wessel 115.41 cubic inches of carbonic acid gas, the weight of which was 78.1192 grains troy. There was likewise found a considerable quantity of water in the vessel, but it was not possible to collect and weigh it. Mr Lavoisier, bowever, estimated its weight at 89.0951 grains; as he concluded, with reason, that the whole of the substances employed were still in the vessel. Now the whole contents of the vessel consisted of carbonic acid gas and water; therefore the carbonic acid gas and water together must be equal to the oxygen gas and alcohol which had been consumed.

But 78.1192 grains of carbonic acid gas contain, according to Mr Lavoisier's calculation \*, 55.279 grains of oxygen: 90.506 grains, however, of oxygen gas had disappeared; therefore 35.227 grains must have been employed in forming water.

35.227 grains of oxygen gas require, in order to form water, 6.038 grains of hydrogen gas; and the quantity of water formed by this combination is 41.265 grains. But there were found 89.095 grains of water in the glass vessel: therefore 47.83 grains of water must have existed ready formed in the alcohol.

\* Mem. Par. 1781.

# ALCOHOL.

6.03 hydrogen 47.83 water

the requisite correction of 76.7 \* and remove stickinger and

Such were the consequences which Mr Lavoisier drew from his analysis. He acknowledged, however, that there were two sources of uncertainty, which rendered his conclusions not altogether to be depended upon. The first was, that he had no method of determining the quantity of alcohol consumed, except by the difference of weight in the lamp before and after combustion; and that therefore a quantity might have evaporated without combustion, which, however, would be taken into the sum of the alcohol consumed. But this error could not have been great; for if a considerable quantity of alcohol had existed in the state of vapour in the vessel, an explosion would certainly have taken place. The other source of error was, that the quantity of water was not known by actual weight, but by calculation.

To this we may add, that Mr Lavoisier was not warranted to conclude from his experiment, that the water found in the vessel, which had not been formed by the oxygen gas used, had existed in the alcohol in the state of water: he was intitled to conclude from his data, that the ingredients of that water existed in the alcohol before combustion; but not that they were actually

> \* Mem. Par. 1781. E e 2

Chap. IV.

Book II. Division II. combined in the state of water, because that combination might have taken place, and in all probability did partly take place, during the combustion.

34 carbon 17 hydrogen

A result certainly far from the truth. From the experiments of Cruikshanks, made by detonating a mixture of the vapour of alcohol and oxygen gas, it follows, that in alcohol the proportion of carbon is to that of hydrogen as nine to one \*. But this is not sufficient to give us the component parts of alcohol with precision.

100

The subject has been lately resumed by Saussure junior, who has published a very elaborate set of experiments on the analysis of alcohol. The alcohol which he employed was obtained by Richter's process, and, of course, of the specific gravity '792, at the temperature of 68°. He employed three different methods of analysis; the first method was similar to that of Lavoisier. He burnt a quantity of alcohol in common air mixed with oxygen gas, and ascertained the weight of alcohol and oxygen consumed. The only sensible products were carbonic acid and water, the first of which he-

\* Nicholson's Journal, v. 205 ..

> carbon 36.890 hydrogen 15.814

# 100.000 the state of the state

He found, that when a considerable quantity of alcohol was burnt, and the water formed collected, it contained a portion of ammonia. Hence he concluded that azote is one of the constituents of alcohol.

His second method of analysis was to mix the vapour of alcohol with oxygen gas when the thermometer stood about 70°, and to detonate the mixture by means of electricity. He estimated the quantity of alcoholic vapour present by means of Mr Dalton's formula, explained in another part of this Work. To make the mixture capable of detonating, he was obliged to add a small quantity of hydrogen gas. The result of the experiment was, that 18°19 grains of alcohol in the state of vapour consumed 75°88 cubic inches of oxygen gas. There were formed 46°69 cubic inches of carbonic acid gas, together with a portion of water. From these data he calculated the component parts of alcohol as follows:

\* The weights and measures mentioned in these experiments are Brench.

+ Nicholson's Jour. xxi. 225.

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merza to

Book II. Division II.

Harrol. The Ellow-

oxygen	37.36	dit bas	. had	gerage.
carbon	46.82	- iluan	2 ( <b>3 1 1</b>	ai with
hydrogen	15.82	gista	3.54	bomne

#### 

This result differs from the preceding, and ought to be more accurate. It deviates, however, very far from the conclusions drawn by Cruikshanks from a similar set of experiments.

The third method of analysis was to decompose the alcohol by passing its vapour through a red hot porcelain tube : the products were a little charcoal, a little oil, partly in crystals, partly fluid, a portion of water holding in solution acetic acid, ammonia, and another acid which resembled benzoic, and a great quantity of heavy inflammable air, to which Saussure gave the name of oxycarbureted hydrogen gas, and which, from his analysis, he considered as a quadruple compound of oxygen, carbon, hydrogen, and azote. The following is the composition of alcohol as deduced from that ana-

lysis :	oxygen	37.85
	carbon	43.65
	hydroge	n 14.94
	azote	3.52
	ashes	0.04
		100.00+

These results, though probably as exact as the present state of our knowledge will enable us to go, are not to be considered as exact. The absolute alcohol of Rich-

\* Nicholson's Jour. xzi. 259.

/ + Ibid. p. 265.

be weights

ter doubtless contains a portion of water; and our ignorance of the quantity renders every attempt to analyse alcohol uncertain. I do not consider the analysis of the oxycarbureted hydrogen as made by Saussure to be exact. The proportion of azote which he infers was probably an error in the experiment. The presence of animonia, however, in the water from alcohol, seems to be a proof that azote actually exists in alcohol, though the proportion of it is so small that it may have been derived from some foreign body accidentally present.

That it contains oxygen, has been proved by a very ingenious set of experiments performed by Messrs Fourcroy and Vauquelin. When equal parts of alcohol and sulphuric acid are mixed together, the sulphuric acid suffers no change; but the alcohol is decomposed, being partly converted into water and partly into ether. Now it is evident that the alcohol could not have been converted into water unless it had contained oxygen \*.

# SECT. II.

#### OF ETHER.

WHEN alcohol is mixed with sulphuric acid and several other acids, and the action of the acid is assisted by heat, the alcohol is decomposed, and converted partly

\* Nicholson's Jour. i. 391.

Chap. IV.

#### COMPOUND COMBUSTIBLES.

Book II. Division II Warities of ether. into a very light volatile fragrant liquor, known by the name of *ether*. The properties of the ether obtained are supposed to vary a little according to the acid employed: accordingly every particular kind is distinguished by the acid used in its preparation. Thus the ether obtained by means of sulphuric acid is called *sulphuric ether*; that by means of nitric acid, *nitric ether*. It will be proper to consider each of these species separately,

# I. SULPHURIC ETHER,

History.

The method of making sulphuric ether is described in the dispensatory of Valerius Cordus, published at Nuremberg about the year 1540; from which Conrad Gesner transcribed it into his *Thesaurus Euonymi de Remediis Secretis*, published in 1552, where it is called *Oleum Vitrioli dulce*\*. It appears to have been known,

\* Whoever will consider the formula given for preparing this Oleum Vitriol dulce by Gesner, will be satisfied that it was very different from the dulcified acids of the moderns, and that it must have been a mixture of alcohol, ether, and sweet oil of wine. The following is the passage of Gesner, as quoted by Hoffman, from whom has been taken the historical facts respecting the knowledge of ether possessed by the alchymistical writers. " Recipe vini ardentis acerrimi & ter sublimati uncias" quinque, olei vitrioli austeri tantundem, misce in venetiano vitro, & pone lin cucarbitam parvant angusto orificio, & luto optimo orificium claude, dimitte ita per integrum mensem aut duos. Deinde effunde in cucurbitam, cui sit immediate annexum alembicum, cujus figuram subjiciemus, pone deinde in parvam fornacem, ac dimidiam ejus partem cinere obrue, postea applica recipientem & luto juncturam claude diligenter, & extrahe uncias sex vini ardentis quas infudisti. Ut vero tutius hoc fiat, pone in halneum Mariæ; sic solum vinum ab-que oleo ascendet. Cum extraxeris autem per balneum infusas uncias sex vini usti, pone id, quod residuum

10

though not in a state of purity, both to Basil Valen- Chap. IV. tine and Paracelsus. But in the writings of chemists published about the end of the 17th century, I have not been able to find any traces of it \*, except in those of Mr Boyle. He was evidently acquainted with it, as appears from different passages of his writings +, though he no where describes it particularly. But it was a paper in the Philosophical Transactions for 1730, by a German who called himself Dr Frobenius, describing several of its most singular properties, that first drew the attention of chemists to this curious liquor ‡. In this paper it first received the name of ether. The German chemists long distinguished it by the name of naphtha.

1. Sulphuric ether is usually prepared by the follow- Preparaing process ||: A mixture of equal parts of alcohol and

tion.

est, in fornacem, ut arena mediam cucurbitæ partem attingat, ac novo & vacuo recipiente eoque non magno applicato, luto juncturam diligenter claude. Accende deinde modestum ignem, & sensim extrahe omnem humiditatem quæ relicta est in cucurbita, donec vihil humidi amplius in fundo appareat; adhibita semper maxima cura & diligentia, ut ignem ita modereris, ne ebulliat usque ad alembici canalem. Nam si hune ebullitio attigerit, sedare non potes, neque prohibere, quin in receptaculum egrediatur, ac totum oleum perdat; solet enim facillime ebullire. Tum videbis duo contineri in co, aqueum videlicet humorem ac pinguem ; segregabis vero unum ab altero statim, ita ut nihil aqueum in oleo relinquatur, nam aqua illa oleum corrumpit; segregatum oleum usui reserva."

\* The Oleum Vitrioli dulce of Lemery, for instance, is very different. from that described by Gesner. (See his Cours de Chymie, p. 502.)

+ See Shaw's Boyle, i. 530. and i. 269; where the process for making ether, and some of its most remarkable properties, are detailed at length.

† Phil. Trans. xxxvi. 283. This paper is little else than a rhapsody in the alchymistical style. At the end of it there is a note by Mr Godfrey (Hankwitz), Mr Boyle's operator, mentioning the experiments formerly made upon it by Mr Boyle and Sir Isaac Newton.

|| Frobenius' process was first published in the Philosophical Transactions, yol. xli.

## COMPOUND COMBUSTIBLES.

Book II. Division II. sulphuric acid is put into the retort, to which a large receiver is then luted. It is proper to surround the receiver with ice, or at least with cold water. Heat is applied; and as soon as the mixture boils, the ether comes over and is condensed, and runs in large strize down the sides of the receiver. As soon as it amounts to one half of the alcohol employed, the process must be stopt. The ether thus obtained is not quite pure, almost always containing a little sulphurous acid.

This acid may be separated by pouring the ether on a little potash, and distilling it over again by means of a moderate heat. Mr Dizé affirms that black oxide of manganese produces this effect still more completely than potash. All that is necessary is to mix a quantity of this black oxide in powder with the impure ether, and to let it remain for some time, agitating it occasionally. The sulphurous acid is converted into sulphuric, and combines with the manganese. The ether is then to be distilled over by the heat of a water bath<sup>\*</sup>.

The separation of the liquid from the sulphurous acid, with which it is mixed, is called the *rectification* of the ether. The usual method, and I may add the best, is the following, first employed by Mr Wolfe: Fill three-fourths of a bottle with the impure ether, add a little water and a portion of slacked lime. Agitate the bottle with violence, and keep it for some time in water before taking out the cork. If the smell of the acid be not removed, add a little more lime, and agitate a second time. Decant off the ether into a retort, and distil it over  $\ddagger$ .

\* Jour. de Phys. alvi. 298.

+ Proust, Ann. de Chim. xlii. 256.

The ether procured by this process is not quite pure, even after all the acid has been removed. The first portion of liquid that comes over during the distillation is merely alcohol impregnated with a little ether. Common ether is in reality a mixture of ether and alcohol. The usual method of separating this liquid is by mixing the ether with water, and then proceeding to distillation with a very moderate heat. But Mr Lowitz has shown that this method does not succeed. The following process yielded him an ether much purer than any that had been previously obtained. Into 16 parts of ether, of the specific gravity '775 in the temperature of 60°, he threw dry powdered salt of tartar, till the last portions were no longer wetted by the liquor. The mixture being allowed to digest, the ether was then drawn off. Its specific gravity was now only .746. By this means it was deprived of the water which it contained. To remove, the alcohol, dry powdered muriate of lime was thrown into the liquid in the same manner, as long as it would dissolve. On standing, the mixture separated into two portions; the alcohol holding the salt in solution sunk to the bottom; the ether swam on the surface. When separated from the inferior liquor, its specific gravity was now only .632 in the temperature of 60°. It was therefore much purer than any former ether described. by chemists, since it never before had been procured lighter than 0.725\*. The ether thus prepared contains a little of the salt, from which it may be freed by distillation. But in that case its specific gravity in-

\* Lowitz, Crell's Annals. 1796, i. 429.

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Book II. Division II. Properties,

creases. The reason seems to be, that the purest portion of the ether assumes the form of elastic fluid.

2. Ether thus obtained is a limpid and colourless liquor, of a very fragrant smell, and a hot pungent taste.

It is so volatile that it can scarcely be poured from one vessel to another without losing a considerable portion of it by evaporation. When poured out in the open air, it disappears in an instant; and during its evaporation produces a very considerable degree of cold. If a glass vessel containing water, and surrounded with a cloth, be dipt into ether, two or three times, and the ether each time be allowed to evaporate from the cloth, the water in the glass freezes. In the open air ether boils at 98°, and in a vacuum at  $-20^\circ$ . Were it not therefore for the pressure of the atmosphere it would always exist in the gaseous state.

When exposed to the open air it speedily assumes the gaseous form. This happens, for instance, if a little of it be poured into a glass phial. The vapour of ether displaces a considerable portion of the air of the phial, and is not soon dissipated. Ingenhousz has shown that the specific gravity of this vapour is very considerable \*.

Mr Dalton has found it 2.25, the specific gravity of common air being 1. According to the estimate of Saussure at the temperature of  $72\frac{1}{2}^{\circ}$ , two French ounces of ether, when converted into vapour, occupy the space of about a French cubic foot  $\ddagger$ . If this estimate be correct, 100 cubic inches of etherial vapour at that tem-

<sup>\*</sup> See his Nouvelles Experiences, p. 180.

<sup>+</sup> Nicholson's Jour. xxi. 335.

perature weigh only 45.15 grains troy, which would make its specific gravity only 1.45. This estimate is greatly below that of Mr Dalton, and in all probability below the truth.

Ether, when exposed to a cold of -46°, freezes and crystallizes †.

3. Neither oxygen gas nor common air produce any effect upon ether in moderate temperatures; but in high temperatures the case is very different. Ether is exceedingly inflammable, and when kindled in the state of vapour burns with rapidity, with a fine white flame, and leaves behind it a trace of charcoal. During its combustion carbonic acid is generated. How well soever it has been rectified, it always exhibits traces of sulphuric acid ‡.

When ether is admitted to any gaseous body standing over mercury, it always doubles the bulk of the gas, as Dr Priestley first observed. If oxygen gas, thus expanded by ether, be presented to a lighted candle, the ether burns with great rapidity, but produces no explosion. But if one part in bulk of this expanded oxygen be mixed with three parts of pure oxygen gas, and kindled, a very loud explosion takes place: the products are water and  $2\frac{1}{2}$  parts of carbonic acid \*. Mr Cruikshanks, to whom we are indebted for this instructive experiment, ascertained, that one part of the vapour of ether takes 6.8 parts of oxygen gas to consume it completely; and from the relative proportions of the

\* Cruikshanks, Nicholson's Journal, v. 205.

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<sup>+</sup> Fourcroy and Vauquelin, Ann. de Chim. xxix. 289

<sup>\$</sup> Scheele, ii. 108.

Book II. Division II. two products, he has shown that the carbon which ether contains is to its hydrogen as five to one.

According to Dalton, one part of ether by weight requires for its combustion 3 parts of oxygen; the products are  $1\frac{3}{4}$  parts of water, and  $2\frac{1}{4}$  of carbonic acid 1. Saussure junior has lately endeavoured to ascertain the constituents of ether, by mixing a known quantity of etherial vapour with oxygen gas, detonating the mixture, and estimating the proportion of oxygen consumed and of carbonic acid formed. The following is the result of his experiments. Ether is composed of

Composition.

> carbon 58.2 hydrogen 22.14 19.66 oxygen

# 100.00 || 00.00 is south 00.001

and Reaves Belling in a

ointen Casterington

What renders this result not to be implicitly depended on is, the probability that the ether of Saussure, which was of the specific gravity 0.717, still contained a portion of alcohol. We see from it, however, that sulphuric ether contains much less oxygen and much more carbon and hydrogen than alcohol.

Ingenhousz was the first who ascertained that the vapour of ether detonates with common air and oxygen gas. His account of the experiment was first published. in a letter to Dr Priestley, in one of the original volumes of that philosopher on Air, and likewise in the 69th volume of the Philosophical Transactions. His method was exceedingly simple. A single drop of

<sup>\$</sup> New System of Ghemical Philosophy, i. 95.

Nicholson's Journal, xxi. 328.

## ETHER.

ether, let fall into a bottle holding about 10 cubic inches of air, gives it the property of detonating. Too much ether destroys the detonation. With oxygen gas the same method succeeds \*.

When ether in the state of vapour is made to pass through a red hot porcelain tube, it is decomposed completely, and a great quantity of carbureted hydrogen gas is obtained  $\ddagger$ . Saussure junior has lately repeated the experiment with precision. He passed 1103 parts of the ether through a red hot porcelain tube; the products were as follows:  $5\frac{1}{4}$  parts of charcoal in the tube, 3 parts of volatile oil crystallized in thin scales and smelling of benzoin; 43 parts of a volatile oil nearly black, partly fluid and partly of the consistence of honey; 3 parts of water and 948 parts of heavy inflammable air. The loss amounting to 100.75 parts was chiefly owing to the escape of oil in the state of vapour  $\ddagger$ .

4. Ether does not combine with water in any proportion : when the liquids are shaken together, they separate again ; but the water retains a portion of the ether, while the ether on the other hand remains united to a part of the water. From the experiments of the Count de Lauraguais, we learn that ten parts of water take up one of ether §. Alcohol, on the other hand, unites with ether in any proportion whatever.

- \* See Ingenhousz' Experiences, p. 171.
- + Dutch Chemists, Jour. de Pbys. xlv. 184.
- \$ Nicholson's Journal, xxi. 323.

§ Mem. Par. 1758. From his experiments it seems to follow, that the portion taken up by water is not other, but a substance which may be obtained in crystals by evaporation.

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## COMPOUND COMBUSTIBLES.

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5. Of the simple combustibles, ether seems to act only on phosphorus and sulphur.

Is is capable of dissolving a small proportion of phosphorus. The solution is transparent; but the addition of a little alcohol to it renders it milky. This furnishes us with a method of ascertaining whether ether be sophisticated with alcohol ‡.

Ether was supposed incapable of acting on sulphur, except when both were in the state of vapour, according to the experiments of Lauraguais; but Favre has shown that a solution may be obtained by digesting flowers of sulphur in cold ether, and that the solvent power of the ether is promoted by exposure to the light. By a month's digestion, he dissolved nearly one part of sulphur in 12 of sulphuric ether; the solution was nearly colourless, but had the taste and smell of sulphureted hydrogen  $\dagger$ .

6. Ether has no action on metals, but revives those that have a weak affinity for oxygen when mixed with their solution in acids, as gold and silver. It dissolves the muriate of gold and the oxymuriate of mercury.

7. It is probable that it has no action on fixed alkalies and earths; but it combines, or at least mixes readily with ammonia.

It absorbs nitrous gas in considerable quantity.

Action of acids. 8. Sulphuric acid seems capable of converting it into a peculiar kind of oil known by the name of sweet oil of wine.

If we fill a bottle capable of holding three or four

1 Micholications

† Brugnatelli, Ann. de Chim. xxiv. 73. † Gehlen's Jour. iv. 227.

English pints with oxymuriatic acid gas, taking care to expel the water as completely as possible, and then throw into it about a dram, or half a dram, of good ether, covering its mouth immediately with a piece of light wood or paper, in a few seconds white vapour will be perceived moving circular in the bottle : this will be soon followed by an explosion accompanied with flame ; at the same time a very considerable quantity of charcoal will be deposited, and the bottle will be found to contain carbonic acid gas \*. The action of the other acids upon ether has not been examined with attention.

9. Ether dissolves the fixed and volatile oils, bitumens, those at least which are fluid, and resins; but it does not act upon gum +.

10. Chemists entertained various opinions respecting Theories of the nature of ether. Macquer supposed that it was tion. merely alcohol deprived by the acid of all its water. But it was generally believed that the acid entered partly into its composition. Scheele published a set of experiments on ether in 1782 ‡; from which he drew as a consequence, that during the process the alcohol is deprived of phlogiston. These experiments were varied, and carried still farther by Pelletier; who adopted the theory of Scheele, modified according to the discoveries of Lavoisier. According to him, ether is alcohol combined with oxygen. This theory was embraced by the greater number of chemists; and it was supposed that the alcohol obtained the new dose of oxygen from

\* Cruikshanks, Nicholson's Jour. v. 205. + Elemens de Chymie by the Dijon Academy, iii. p.313 t Scheele, ii. 105. Vol. II. Ff

its composi-

Chap. IV.

Book II. Division II. the sulphuric acid. But the formation of ether has been lately examined with much care by Fourcroy and Vauquelin. These ingenious chemists have concluded from their experiments, that during the process the alcohol is completely decomposed, and that ether is composed of the same ingedients as alcohol, but combined in different proportions. Ether, according to them, contains a greater proportion of hydrogen and oxygen, and a smaller proportion of carbon than alcohol \*.

The theory of these chemists was disputed by Laudet + and Dabit 1, who endeavoured to prove that oxygen is always necessary for the formation of ether-This they did by repeating the experiments on ether which had been formerly made by Scheele. They distilled a mixture of sulphuric acid, black oxide of manganese, and alcohol. The sulphuric acid was not decomposed, as in common cases, no charcoal was deposited, no gas came over, the black oxide lost part of its oxygen, and the quantity of ether obtained was greater than usual. According to Dabit, ether contains a smaller proportion of hydrogen, and a greater proportion of oxygen and carbon, than alcohol. These objections were almost immediately answered by Fourcroy and Vauquelin, who proved that ether obtained by means of the black oxide of manganese possesses very different properties from sulphuric ether. Consequently its formation and composition cannot destroy their conclusions respecting the formation and composition of sulphuric ether §. From the preceding analysis of Saus-

<sup>\*</sup> Ann. de Chim. xxiii. 203, and Nicholson's Jour. i. 391. † Ann. de Chim. xxxiv. 282. § Ibid. 319.

## ETHER.

sure it follows, that ether contains less oxygen than al- Chap. IV. cohol, but more carbon and hydrogen.

11. As the action of sulphuric acid on alcohol, and Action of the formation of ether, is one of the most interesting cid on alco phenomena in chemistry, and as it may enable us to form more precise ideas, both respecting the composition of alcohol and ether, it will be proper to examine it with attention.

When four parts of sulphuric acid and one part of I. Olefant, alcohol are mixed together, and a moderate heat applied, the mixture blackens, boils violently, and a great quantity of gas is disengaged. This gas, which was first examined by the Dutch chemists, received from them the name of olefiant gas. It has been described in a former part of this Work, under the name of supercarbureted hydrogen \*.

What remains in the retort after the disengagement of this gas is chiefly sulphurous acid blackened with charcoal, and probably also some vegetable acid.

When equal parts of sulphuric acid and alcohol are 2. Orable mixed together, the phenomena which take place are considerably different. If the mixture be made cautiously, and allowed to remain at the common temperature for about 30 hours, crystals of oxalic acid often form in it t.

A combination of two parts of sulphuric acid and one of alcohol elevates the temperature to 201°, becomes immediately of a deep red colour, which changes to a black a few days afterwards, and emits a smell perceptibly ethereal.

\* See Vol. I. p. 56:

+ Cadet, Jour. de Pbys. li. 232. Ff2

acid.

sulphuric a-

Book II.

a Ether.

When a mixture of equal parts of alcohol and sulphuric acid is exposed to the action of heat in a proper apparatus, the following phenomena take place, as has been ascertained by Fourcroy and Vauquelin.

When the temperature is elevated to 208°, the fluid boils, and emits a vapour which becomes condensed by cold into a colourless, light, and odorant liquor, which from its properties has received the name of *ether*. If the operation be properly conducted, no permanent gas is disengaged until about half the alcohol has passed over in the form of ether. Until this period there passes absolutely nothing but ether and a small portion of water, without mixture of sulphurous or of carbonic acid.

If the receiver be changed as soon as the sulphurous acid manifests itself, it is observed that no more ether is formed, but the sweet oil of wine, water, and acetous acid, without the disengagement hitherto of a single bubble of carbonic acid gas. When the sulphuric acid constitutes about four-fifths of the mass which remains in the retort, an inflammable gas is disengaged, which has the smell of ether, and burns with a white oily flame. This is what the Dutch chemists have called *olefiant gas*. At this period the temperature of the fluid contained in the retort is elevated to  $230^\circ$  or  $234^\circ$ 

When the sweet oil of wine ceases to flow, if the receiver be again changed, it is found that nothing more passes but sulphurous acid, water, carbonic acid gas; and that the residuum in the retort is a black mass, consisting for the most part of sulphuric acid thickened by carbon.

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## ETHER. CHOMMON

11. From these phenomena Fourcroy and Vauquelin Chap. IV. have drawn the following deductions.

A small quantity of ether is formed spontaneously, Theory of the decomand without the assistance of heat, by the combination position of of two parts of concentrated sulphuric acid and one part sulphuric of alcohol.

As soon as ether is formed, there is a production of water at the same time; and while the first of these compositions takes place, the sulphuric acid undergoes no change in its intimate nature.

As soon as the sulphurous acid appears, no more ether is formed, or at least very little; but the sweet oil of wine passes over, together with water and acetic acid. alle:

The sweet oil of wine having ceased to come over, nothing further is obtained but the sulphurous and carbonic acids, and at last sulphur, if the distillation be carried to dryness.

The operation of ether is therefore naturally divided into three periods : the first, in which a small quantity of ether and water are formed without the assistance of heat ; the second, in which the whole of the ether which can be obtained is disengaged without the accompaniment of sulphurous acid; and the third, in which the sweet oil of wine, the acetous acid, the sulphurous acid, and the carbonic acid, are afforded. The three stages have no circumstance common to all but the continual formation of water, which takes place during the whole of the operation.

A combination of sulphuric acid and alcohol in equal parts does not boil at less than 207° of temperature, while that of alcohol alone boils at 176°. Now since ebullition does not take place till the higher temperature, 453

alcohol by

acid.

## COMPOUND COMBUSTIBLES.

Book H. Division H. it is clear that the alcohol is retained by the affinity of the sulphuric acid, which fixes it more considerably. Now organic bodies, or their immediate products, when exposed to a lively brisk heat, without the possibility of escaping speedily enough from its action, suffer a partial or total decomposition, according to the degree. of temperature. Alcohol undergoes this last alteration when passed through an ignited tube of porcelain, The reason therefore why alcohol is not decomposed when it is submitted alone to heat in the ordinary apparatus for distillation is, that the temperature at which it rises in vapours is not capable of affecting the separation of its principles ; but when it is fixed by the sulphuric acid or any other body, the elevated temperature it undergoes, without the possibility of disengagement from its combination, is sufficient to effect a commencement of decomposition, in which ether and water are formed, and carbon is deposited. Nothing more therefore happens to the alcohol in these circumstances than what takes place in the distillation of every other vegetable matter, in which water, oil, acid, and coal, are afforded.

Hence it may be conceived that the nature of the products of the decomposition of alcohol must vary according to the different degrees of heat; and this explains why at a certain period no more ether is formed but the sweet oil of wine and acetous acid. In fact, when the greatest quantity of alcohol has been changed into ether, the mixture becomes more dense, and the heat which it acquires previous to ebullition is more considerable. The affinity of the acid for alcohol being increased, the principles of this acid become separated; so that, on the one hand, its oxygen seizes the

#### ETHER.

hydrogen, and forms much water, which is gradually volatilized; while, on the other, the ether retaining a greater quantity of carbon, with which at that temperature it can rise, affords the sweet oil of wine. This last ought therefore to be considered as an ether containing an extraordinary portion of carbon, which gives it more density, less volatility, and a lemon-yellow colour.

Such is the ingenious explanation of the formation of sulphuric ether proposed by Fourcroy and Vauquelin. They have succeeded completely in proving that the opinions formerly entertained respecting that singular process were erroneous; though their own explanation is not sufficiently precise to enable us to ascertain exactly the component parts of ether.

## II. NITRIC ETHER.

NATRIC ether is first mentioned in an epistle written by Kunkel to Voight, and published in 1681\*; but no attention was paid to it by succeeding chemists till it was discovered a second time by Naviet in 1742 +, and a third time by Sebastiani in 1746 1.

The method of preparing it, proposed by Navier, Preparawas this : Twelve parts of alcohol are put into a strong bottle, which is kept surrounded with water, or rather with ice: eight parts of nitric acid are poured in at intervals, the mixture being agitated after every addition. The bottle is then well corked, and the cork se-

Chap. IV.

\* Epistola contra Spiritum Vini sine Acido. + Mem. Par. 1742. 1 Diss. de Nitro, 1746,

cured by leather. Ether gradually forms at the surface of the liquid. After five or six days, when the formation is supposed to be over, the cork is to be pierced with a needle, to allow a quantity of nitrous gas to escape, which would otherwise carry the ether along with it. The cork is then to be drawn; the whole liquid is to be poured into a funnel, and by means of the finger the liquid below is allowed to run out while the either is retained.

This method is somewhat hazardous; for the quantity of nitrous gas evolved is so great as often to burst the bottle. Dr Black substituted in place of it a very ingenious process. He put into a glass phial the proper quantity of nitric acid; over this was poured gently a stratum of water, and the alcohol was poured over all. Thus there were three strata of liquids in the vessel: the acid lowermost, and the alcohol uppermost, separated from each other by the water. The acid and alcohol gradually combined with the water, and coming into contact acted on each other without violence; and thus the ether was formed without risk.

Dehne has given another process for obtaining nitric ether exceedingly tedious, but not attended with any risk. The alcohol is put into a tubulated retort, to which a large receiver is luted;  $\frac{1}{48}$ th part of nitric acid is to be added every four hours, drop by drop, till it amounts to about half the weight of alcohol; then the mixture becomes hot, and ether passes over into the receiver. After this a little more nitric acid is to be added every morning and evening. Ether gradually forms on its surface. The acid is to be added till it falls down to the bottom of the retort in the form of

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#### ETHER.

green globules, indicating the perfect saturation of the chap. IV. acid with nitrous gas. This is a proof that no more ether will be formed.

Various other methods of preparing nitrous ether have been proposed by chemists, as the distillation of a mixture of sulphuric acid, nitre, alcohol, &c. But the process preferred by artists is that of Chaptal as corrected by Proust. A large retort is huted to a glass globular vessel furnished with a tube of safety. From this globe a tube passes to a second, likewise furnished with a tube of safety; and to this last vessel is connected three Woulfe's bottles in the usual way, which must be half full of alcohol. A mixture of 32 parts of alcohol and 24 of acid, of the specific gravity 1.3, is put into the retort. The heat of a chaffing dish is applied, and removed as soon as the effervescence begins. The greatest part of the ether is detained by the alcohol in the first Woulfe's bottle. This mixture is to be saturated with an alkali, and the ether separated by distillation \*.

These processes are all of them so defective and complicated, that little precise knowledge was acquired of nitric ether, till Thenard undertook an investigation

\* Proust, Ann. de Chim. xlii. 262.—Brugnatelli has proposed the following method; but I find that the proportion of ether obtained by it is much smaller than the other processes, though Brugnatelli affirms the reverse. Put an ounce of sugar into a retort, and pour over it two ounces of alcohol. Lute to it a large receiver with slips of paper, and then add three ounces of nitric acid. The sugar is dissolved, the mixture boils, and the ether passes over pure, equal in weight to the alcohol. See Jour. de Chim. iii. 68.—Perhaps my want of complete success was owing to the use of a stronger acid than that employed by Brugnacelli. 457

Thensel's

of it in 1807. He distilled a mixture of alcohol and nitric acid, and carefully collected and examined all the products both liquid and gaseous. A considerable part of the ether formed he found made its escape in the gaseous form, while the liquid in the receiver, hitherto considered nitric ether, was a mixture of alcohol, water, ether, nitrous, and acetic acids. These results led him to the following method of procuring pure nitric ether.

Thenard's process.

Equal weights of alcohol and nitric acid, of the specific gravity 1.283, were put into a retort. To the beak of the retort was luted a glass tube, which plunged to the bottom of a long narrow glass jar half filled with a saturated solution of common salt in water. From the top of this jar passed another tube, which went to the bottom of another similar jar, likewise half filled with a solution of common salt. In this manner five similar jars were connected with each other, each half filled with a saturated solution of common salt. From the last a tube passed to a water trough to receive the gaseous products in proper jars. Each of these five jars was surrounded with a mixture of snow and salt to keep it as cool as possible. A moderate heat being applied to the retort a violent effervescence It was found necessary to withdraw the fire, began. and even to moisten the outside of the retort with water. in order to prevent the vessels from bursting. The gaseous matter evolved was thus forced to pass through the different jars containing the common salt solution, and there it deposited the greatest part of its ether, The ether was found floating on the surface of the solutions in each, but the greatest part of it in the first sar. It was separated; and to free it from the nitrous

#### ETHER.

and acetic acids with which it was contaminated, it was agitated in a close phial with a sufficient quantity of chalk, till it ceased to produce any change on vegetable blues. It was then decanted off. Thus purified it possessed the following properties.

It had a slightly yellow colour, and a very strong Properties of nitric etherial odour. Its taste was strong and quite peculiar. ether. It was rather heavier than alcohol, but much more volatile than sulphuric ether. Hence it only moistened bodies for a moment, and produced a very considerable degree of cold by its evaporation. The heat of the hand was sufficient to set it a boiling.

It was lighter than water, and required 48 parts of that liquid to dissolve it, and communicated to it an odour like that of apples. It dissolved in alcohol in every proportion. It burnt very brilliantly with a white flame like sulphuric ether. When kept for some time, both nitrous and acetic acids were formed in it. The same acids were evolved if the ether was heated, or if it was agitated with water. When brought in contact with a little of these acids, it instantly absorbed them, and acquired the property of converting vegetable blues into red.

When brought in contact with nitrous oxide, or any other gas, at the temperature of 70°, it instantly quintupled its bulk, being converted into vapour. At that temperature its vapour was capable of supporting a column of mercury 28.74 inches high. At the temperature of 70°, and when the barometer stands at 30 inches, it is liquid; but if we increase the heat or diminish the pressure, it assumes the state of vapour. It is much more elastic than sulphuric ether. At the temperature of 70°, the vapour of sulphuric ether is capa-

Chap. IV,

ble of sustaining a column of mercury only 16 inches high.

Such are the properties of nitric ether ascertained by Thenard \*. They show us that it differs essentially from sulphuric ether. The gradual evolution of nitrous acid in it, demonstrates that it must contain azote as one of its constituents. Thenard endeavoured to ascertain the proportion of its constituents by passing it through a red hot porcelain tube, and examining the new substances evolved. They were water, carbonic acid, charcoal, oil, and a considerable quantity of a gas which contained azote and nitrous gas, and a heavy inflammable air, which detonated with oxygen, and yielded carbonic acid and water. A little ammonia appeared also to have been produced. By estimating the weight of each of these substances and their constituents, Thenard concluded, that 100 parts of nitric ether were composed of

Composi-

48.52 oxygen 28.45 carbon 14.49 azote 8.54 hydrogen

## 100.00 +.

But this analysis is liable to several exceptions. There was a considerable loss, and the composition of several of the substances evolved is not sufficiently determined. A better mode of analysis would have been, to have mixed the vapour of the ether with a sufficient quantity of oxygen, and to have decomposed it by electri-

\* Mem. d' Arcueil, i. 75.

+ Ibid. i. 360.

#### ETHER.

city. By this method, knowing the specific gravity of Chap. IV. the vapour, and the products furnished by its decomposition, it would have been easy to have deduced its constituents.

During the formation of nitric ether a vast quantity Gascous of gas is evolved. The Dutch chemists examined this gas, and considered it as a compound of nitrous gas and ether; but Thenard has shown, that it is much more complicated in its nature. The result of his examination is, that it consists chiefly of nitrous oxide gas, mixed with a little nitrous gas, azote, carbonic acid, acetic acid, nitrous acid, and a considerable proportion of etherial vapour. But the proportion of this last ingredient diminishes according to the degree of cold to which it has been subjected.

After the mixture of alcohol and nitric acid has Andresidue ceased to give out ether, there remains in the retort about three-fifths of the original quantity. This residue Thenard also subjected to examination. It has a yellow colour and an acid taste. It consists chiefly of water, holding in solution some nitric acid, some alcohol, a very small portion of acetic acid, and a matter which Thenard could not separate, but which very readily assumed the state of charcoal.

Thus it appears, that both the alcohol and acid are decomposed during the process of making nitric ether. and that the constituents of both enter into the composition of the ether formed. We are not sufficiently acquainted with the composition of alcohol, and with the proportion of the other ingredients evolved, to be able to enter into the minutiæ of the decomposition. Some light may be thrown upon the subject by a careful ex-

products,

examined.

Book II. Division II.

Action of nitric acid on alcohol. amination of the phenomena which take place during the action of nitrie acid on alcohol.

1. When equal parts of alcohol and nitric acid are mixed, a violent effervescence takes place; spontaneously if the acid be concentrated; on the application of heat if the acid be diluted. This effervescence is owing to the emission of the gas, which the Dutch chemists considered as a mixture of ether and nitrous gas, but which Thenard has shown to consist chiefly of nitrons oxide and ether. The Dutch chemists have called it *nitrous etherized gas*\*.

z. Nitrous etherised gas.

2. Oxalic acid. This gas has a disagreeable ethereal odour : it burns with a yellow flame; is completely absorbed by water, alcohol, and the solution of potash; ammonia has no action on it. When fired along with oxygen gas it detonates. Sulphuric, sulphurous, nitric, and muriatic acids, decompose it.

-2. When one part of alcohol and three parts of nitric acid, of the specific gravity 1.261, are mixed together, and a very moderate heat applied, a great quantity of gas is disengaged, which consists chiefly of nitrons etherised gas and nitrous gas. When only  $\frac{1}{32}$  d part of the liquid remains in the retort, if it be allowed to cool, a number of crystals of oxalic acid are formed +. By this process 1.167 parts of oxalic acid may be obtained from 16 parts of alcohol  $\ddagger$ .

Combustion of alcohol. 3. When one part of nitric acid is poured upon its own weight of alcohol, and one part of sulphuric acid is added a little after, the mixture takes fire and burns

\* Jour. de Pbys. xlv. 245. \$ Sage, Jour. de Pbys. 1. 346. + Scheele and Hermbstadt.

with great rapidity. When this experiment is performed in close vessels, the products are ether and oil, besides what remains in the vessel in which the combustion takes place \*.

4. When nitric acid, partly saturated with mercury, is poured upon alcohol, and heat applied, the products are nearly the same, but the phenomena are very different. The curious appearances which accompany this mixture were first observed and explained by Mr Howard +. The process, as described by him, is as follows: Dissolve, by means of heat, 100 grains of mercury in a measured ounce and a half of nitric acid, of the specific gravity of about 1.3. Pour this solution upon two measured ounces of alcohol, and apply heat till the mixture begins to effervesce. The heat is then to be withdrawn. The action becomes violent, and continues for some time; a dense white smoke issues from the vessel, which is heavier than the atmospheric air, and may be poured into glass jars, where it continues for some time like fine white clouds. Mr Howard has made it probable that this fume is composed of etherised nitrous gas holding oxide of mercury in solution. Meanwhile a white powder falls to the bottom of the mixture. When the effervescence is over, this white powder is to be separated by filtration, washed with pure water, and dried in a heat not exceeding 212°.

Mr Howard has examined the properties of this powder, which has the appearance of minute crystals. He has given it the name of *fulminating mercury*.

\* Brugnatelli, Ann. de Chim. xxix. 327.

+ Nicholson's Journal, iv. 173.

Chap. IV.

Howard's fulminating mercury.

When heated to the temperature of 368°, it explodes with considerable violence. The same effect is produced by friction, by the blow of a hammer, by electricity, and by flint and steel. The products, after combustion, are carbonic acid gas, azotic gas, water, and mercury. It produces very violent effects, but only at a small distance. Concentrated sulphuric acid, when poured upon it, causes an immediate explosion; diluted sulphuric acid likewise decomposes it, but without exploding. A gas passes over, which is a mixture of carbonic acid, and of a peculiar inflammable gas which burns with a greenish flame ; the same into which the etherised nitric gas is converted by the action of diluted sulphuric acid. There remains in the sulphuric acid a white powder, consisting of oxalate of mercury and a few globules of mercury \*.

Composition. From the experiments of Mr Howard, it follows that this powder is composed of oxalate of mercury and nitrous etherised gas. But the subsequent analysis of Fourcroy has shown, that it varies in its nature according to the mode of preparing it. When prepared in Howard's way with little heat, it is a compound of nitric acid, oxide of mercury, and a peculiar vegetable substance. When the heat is continued during the whole fermentation, the powder has a greenish colour. It detonates more feebly, and on hot coals emits a blue fame. It is composed in that case of ammonia, oxide

\* Howard, Nicholson's *Journal*, iv. 173. Brugnatelli has announced, that by pouring one ounce of alcohol and one ounce of uitric acid on 100 grains of dry nitrate of silver, (lunar caustic) in a beer glass, a fulminating silver is produced, much more powerful than fulminating mercury. Nicholson's *Jour*, vii. 285.

is a substitution of the a

of inercury, and more of the peculiar vegetable matter. Chap. 1V. When the mixture is boiled for half an hour; the powder is composed of oxalate of mercury and a very small quantity of vegetable matter. It does not detonate, but decrepitates when heated \*. These experiments of Fourcroy enable us to reconcile the seemingly opposite results of Howard and Berthollet +. This sait has been lait

### III. MURIATIC ETHER.

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free from witter as tessible, of the follow

AFTER the discovery of sulphuric and nitric ethers. various attempts were made to obtain ether by the action of muriatic acid on alcohol: But this acid in its usual state is too much diluted with water to act with much energy upon alcohol. It was thought necessary; therefore, in order to procure muriatic ether, to employ the acid in a different state. Two methods have been discovered.

1. Those muriatic salts are chosen which may be ob- Breparas tained dry, and at the same time have a strong affinity tion, for water. All the salts which have been hitherto tried 1. By salts; with success have a metallic base in the state of a peroxide t. The oxymuriates of mercury, iron, arsenic, and antimony, produce ether when distilled with alcohol: but the salt which answers best is the oxymuriate

\* Journal of the Royal Instit. i. 256.

+ According to Berthollet, fulminating mercury is composed of ammonia, oxide of mercury, and altered alcohol, which produces carbonic acid when decomposed. Phil. Mag. xii. 92.

t I distinguish this state of oxidizement in the metallic salts by prefing oxy to the usual names of the salt.

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Vol. II.

a By the

of tin. By means of this salt Courtanvaux formed ether, in 1759, by the following process: Three parts of fuming oxymuriate of tin and one part of alcohol are mixed together; and after the vapours and heat produced have subsided, the mixture is put into a retort, to which two large receivers are attached, and distilled. There comes over first a little alcohol, then the ether\*. This salt has been lately recommended as very proper for making muriatic ether by Klaproth  $\ddagger$ .

2. By the acid.

2. Pure alcohol is saturated with muriatic acid gas as free from water as possible. The following is the formula recommended by Mr Basse. Keep a quantity of common salt for an hour in a state of fusion, in order to deprive it of its water of crystallization. Put 20 parts of this salt into a tubulated retort, to the beak of which is fitted a bent tube, plunging into Woulfe's bottle, containing 10 parts of alcohol as strong as possible.

Introduce into the retort, in small quantities at a time, 10 parts of the most concentrated sulphuric acid, allowing the common air to escape from the bottle containing the alcohol; then distil in a sand bath till the muriatic acid comes over, keeping the alcohol bottle as cool as possible during the process. The alcohol, thus saturated with acid, is put into a retort, and one half of it distilled over. Agitate this portion with an alkaline ley, and then decant off the ether which swims on the surface : it usually amounts to  $2\frac{1}{2}$  parts  $\frac{1}{2}$ .

\* Jour. de Scaw. 1759, p. 549. This process was discovered by Rouelle. See Jour. de Plys. lvi. 219.

+ Crell's Annals, 1796, ii 99.

† Jour. de Chim. iv 85. This method is very similar to the following one given before by Van Mons: Saturate a given quantity of alcohol

F. I.L.

#### ETHER.

Very little was known of the properties of muriatic Chap. IV. ether, till Gehlen published a dissertation on the subject in 1804\*. He employed two processes: 1. the action of the fuming oxymuriate of tin on alcohol; 2. the process of Basse detailed above. Both of them furnished muriatic ether, the peculiar properties of which he has described with accuracy. Thenard published three dissertations on it in 1807 +, pointed out the simplest process for obtaining it, examined the effect of oxymuriates on alcohol, described the properties of muriatic ether in detail, and made a set of experiments to ascertain its constituents. To the dissertations of these two chemists we are indebted for all that we know of this very remarkable substance.

The process recommended by Thenard for procuring Thenard's this ether is the following: Equal bulks of muriatic acid and alcohol, both as strong as possible, are put into a retort. of such a size as not much more than to hold the mixture. A few grains of sand should be put into the retort, to prevent the violent boiling which might otherwise take place. From the beak of the retort a tube passes into a glass jar, twice the size of the retort, and furnished with three mouths. This jar should be half filled with water, of the temperature of about 70°. Into the second mouth

with muriatic acid, by distilling a mixture of two parts of common salt and one part of sulphuric acid into a Woulfe's apparatus containing two parts of alcohol. Mix this saturated alcohol with half a part of black oxide of manganese, and put into the Woulfe's apparatus a solution of pure potash in water, and distil with a low heat. The ether and oxymuriatic acid pass over, and the potash prevents the acid from acting so violently on the ether. See Ann. de Chim. xxxiv. 141. \* Gehlen's Jour. ii. 206.

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+ Memi d' Arcueil, i. 115. 140. 337.

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process.

Book I'. Division II. a straight tube of safety is luted, and into the third a tube, which passes into a water trough to receive the gas. When heat is applied, the mixture soon emits bubbles. There passes into the receiver alcoholwith acid and water; but the whole of the ether makes its escape in the state of gas, and must be received in proper vessels. From 500 grammes of acid and the same bulk of alcohol, between 20 and 30 litres of etherial gas are obtained. Or, in round numbers, a mixture of acid and alcohol, weighing about 30 ounces troy, will yield between 1220 and 1830 cubic inches of etherial gas.

This gas is colourless, it has a strong etherial smell, and a sweetish taste. It produces no change on the infusion of litmus, the syrup of violets, or lime water. Its specific gravity is 2.219, that of air being 1. At the temperature of 64° water dissolves its own bulk of this gas.

Properties of the ether. When exposed to a cold of 52°, it loses its aerial form and becomes liquid ether. It may be procured abundantly in that state by passing it into a dry glass jar surrounded with ice. Muriatic ether, in its liquid state, is colourless like water, very liquid, has no action on vegetable blues, and has the same smell and taste as in the gaseous state. At the temperature of 41°, Thenard found it of the specific gravity 0.874\*. It is much more volatile than alcohol, or even sulphuric ether, assuming the gaseous state when not hotter than 64°.

\* Basse obtained it of the specific gravity 0.820, and Gehlen of 0.845. Here we must consider weight as a mark of purity. Hence it is obvious that the muriatic ether of the German chemists was less pure than Thenard's.

None of the usual tests indicate the presence of any Chap. IV. muriatic acid. It does not affect vegetable blues, nor give out acid when agitated with an alkaline ley, or occasion an immediate precipitate when mixed with nitrate of silver. But when brought in contact with a combustible it burns readily with a green coloured flame, and a very considerable portion of muriatic acid is immediately disengaged in the state of vapour. This very extraordinary fact was first observed by Gehlen : it has been minutely examined by Thenard. When allowed to remain for a long time in contact with an alkali, it does give out a portion of muriatic acid, and it slowly produces a precipitate in nitrate of silver after the interval of several days, and the quantity of precipitate increases with the time. But in neither case is the ether decomposed, or deprived of the property of giving out muriatic acid when burnt.

From the experiments of Thenard it appears, that Composiduring the formation of muriatic ether no gaseous product whatever is evolved but muriatic ether; nor is any other new substance evolved, unless a portion of water may be formed. A portion of the muriatic acid as well as of the alcohol disappears; and when the ether is decomposed, exactly the portion of acid is evolved which had disappeared. It is extremely difficult from these facts to form an accurate notion of the way in which the ether is formed. Is it a compound of alcohol and muriatic acid ?- The little effect which these two bodies have on each other, even when mixed in the state of vapour, renders that opinion unlikely. It is equally difficult to conceive the state of the muriatic acid in that liquid. It seems to be perfectly neutralized, as all its usual properties are concealed ; and it must

tion.

be retained very powerfully, since none of those substances on which it acts with the greatest energy indicate its presence when mixed with the ether. At the same time, difficult as it is to explain how it is concealed, it is more probable that it exists in the state of muriatic acid than decomposed, if we consider how difficult it is to decompose this acid, and how obstinately it has resisted the numerous attempts to ascertain its composition.

Thenard has endeavoured to ascertain the composition of muriatic ether. From the quantity of muriatic acid which disappears during its formation, he has calculated that 100 parts of muriatic ether contain 29.44 of acid; an enormous quantity, since it exceeds the proportion of real acid in the strongest muriatic acid of commerce. By mixing determinate portions of muriatic acid gas with oxygen gas, firing the mixture, and ascertaining the products, which are only carbonic acid and water, he endeavoured to ascertain the proportion of the other constituents. The following is the result of his examination : ....... 29.44 muriatic acid

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If any confidence can be put in this analysis and in that of alcohol by Saussure, we may infer from them, that muriatic ether does not contain the alcohol in the state of alcohol, since the carbon, oxygen, and hydrogen do not bear to each other the same proportion in the e-

\* Mem. D'Arqueil, i. 341. Herralla 20 box

is équally a acid in the

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ther that they do in alcohol. The proportion of carbon in the ether is a good deal more, and that of the oxygen less than in the alcohol. and said to touborg ad I

After the discovery of oxymuriatic acid, Scheele showed that ether might be obtained by distilling a tic acid on mixture of alcohol, black oxide of manganese, and muriatic acid; or by distilling sulphuric acid, common salt, black oxide of manganese, and alcohol : but the quantity which can be obtained by this process is trifling : for the oxymuriatic acid acts upon the ether formed, and converts it into a kind of oil. Indeed, if we believe Mr Basse, ether is never obtained by means of oxymuriatic acid, but merely an oil which sinks in water \*. This has been amply confirmed by the late experiments of Thenard +; from which we may conclude, that oxymuriatic acid converts alcohol into oil, and not into ether, and that which has been taken for ether is nothing else than alcohol holding some of this oil in solution.

## IV. ACETIC ETHER. otash in three parts alcohol, add-

ETHER may be produced also by the action of acetic acid on alcohol. This was discovered by the Count de Lauraguais in 1759 t. He obtained it by distilling a mixture of acetic acid and alcohol with the same precautions as are employed in the distillation of sulphuric berg with the same result. They affirm that mental

The process, as corrected by Pelletier, is as follows : Prepara-Mix together, in a retort, equal quantities of acetic tion. acid (from acetate of copper) and alcohol, and distil over the alcohol. Pour it back into the retort, and di-

\* Jour. de Chim.iv. 88. + Mem. D'Arcueil. i. 47. ‡ Jour de Scav. 1759, F. 324. "专行"的问题。日本的"全主"的

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Chap. IV.

Action of oxymuriaalcohol.

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Book II. Division II. stil a second time. What comes over must be poured back a second time, and subjected to a third distillation. The product of this third distillation is a mixture of acetic acid and ether. Saturate the acid with potash, and distil with a moderate heat. Acetic ether comes over pure \*. Bucholz has given another process, which is much more economical. Put into a retort 16 parts of acetate of lead, six parts of strong sulphuric acid, and nine parts of alcohol. Distil over 10 parts. Agitate this liquid with a third of its bulk of lime-water, and decaut off the ether, which will swim on the surface, It usually amounts to six parts †.

Scheele could not succeed in obtaining ether by Lauraguais' process; most likely because he neglected to return the distilled liquid a sufficient number of times into the retort. But he discovered another, by which it may be obtained without difficulty. Nothing more is necessary than to add a little sulphuric acid to the mixture; or acetic ether may be obtained by dissolving one part of acetate of potash in three parts alcohol, adding more sulphuric acid than is sufficient to saturate the potash, and then distilling ‡.

Schultze, an apothecary at Kiel, has lately repeated the experiments of Scheele, and found them accurate. His experiments were repeated by Gehlen and Lichtemberg with the same result. They affirm that pure acetic acid does not form ether with alcohol, but that ether is formed if there be present the smallest quantity of any other acid §. The subject has been lately examined by Henry || and by Thenard ¶; both of whom have

- . Jour. de Phys. XXVIII. 141.
- \$ Scheele, ii. 117.
- Ann. de Chim. lyiii. 199.
- † Jour. de Chim. iii. 222.
- § Ann. de Clim. lvil. 94.
- ¶ Mem. D'Arqueil, i. 153.

#### Scheele's process.

shown in the most satisfactory manner, that acetic acid Chap. IV. and alcohol yield an ether by the process of Lauraguais s matter is character host det and Pelletier.

Thenard employed nearly equal weights of a very strong acid and alcohol of the specific gravity 0.3056, and repeated the distillation 12 times. No gas of any kind was evolved during the process. He then mixed the whole together, and endeavoured to neutralize the acetic acid by potash. The neutralization succeeded but imperfectly; abundance of crystals of acetate of potash precipitated. By a cautious distillation the acetic ether came over in the first place, and afterwards a portion of alcohol, holding a little ether and acetic acid in solution. By a subsequent distillation off acetate of potash, the acetic ether was obtained perfectly pure. During the formation of this ether a quantity of acid as well as of alcohol disappear; both of course enter into the composition of the ether, or at least their constituents enter.

Acetic ether is limpid and colourless; it has an a- Properties greeable odour of ether and acetic acid. It does not redden vegetable blues. It has a peculiar taste different from that of all other substances, and bearing no resemblance to that of alcohol. Its specific gravity at the temperature of  $44\frac{10}{2}$  is 0.866. It boils at the temperature of 160°. It burns with a yellowish-white flame, and acetic acid is developed during its combustion. It does not undergo any change by keeping. At the temperature of 62° it requires more than 7 times its weight of water to dissolve it.

Though allowed to remain in contact with water, or dissolved in it, no change takes place; but when left in contact with caustic potash, acetic acid is gradually evol-

Book II. Division II. ved, which saturates the alkali. If it be distilled in this state, alcohol comes over very much diluted with water. No gaseous matter is disengaged. Hence it seems to be nothing else than a compound of acetic acid and alcohol. The acid is neutralized in the ether, as it exhibits none of its usual properties.

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SCHEELE and Lavoisier attempted in vain to form ether by means of phosphoric acid. Boudet published a dissertation on the subject much later. By distilling a mixture of phosphoric acid and alcohol he obtained a liquid lighter than alcohol; but it was completely miscible with water, and therefore did not possess the properties of ether \*. The subject has been lately resumed by Boullay, whose experiments were attended with more success. They were published in 1807 †.

Process.

He introduced into a tubulated retort 500 parts of phosphoric acid, obtained by the combustion of phosphorus by nitric acid, vitrified, redissolved, and of the consistence of honey. The retort communicated with a receiver surrounded by a mixture of ice and salt. This receiver communicated with a jar filled with lime water, and from this jar a tube passed to a pneumatic trough. The phosphoric acid was raised nearly to the heat of boiling water ; and then by means of a species of funnel, the tube of which passed through the melted phosphoric acid to the bottom of the retort, 500 parts of alcohol were slowly introduced. The mixture was

\* Ann. de Chim. xl. 123.

† Ibid. lxii. 192.

dissolved is 10. 10

#### ETHER. JUNCO

accompanied by a violent boiling, the phosphoric acid became black, and striæ in abundance appeared on the top and neck of the retort. The distillation was continued till the phosphoric acid became dry. There passed over into the receiver, 1st, 120 parts of alcohol, smelling feebly of ether; 2d, 260 parts of a colourless light liquid, smelling strong of ether; 3d, 60 parts of water saturated with ether, over which swam 4 parts of a yellow liquid very much resembling the sweet oil of wine in appearance; 4th, another liquid of a disagreeable odour, and reddening vegetable blues. When saturated with potash and evaporated, it left a quantity of acetate of potash in crystals. The lime water became milky, but only towards the end of the process. A quantity of gas was obtained which burnt like ether, and seemed to consist chiefly of ether uncondensed to grand off .....

The two first products being rectified on muriate of Properties. lime, furnished 60 parts of a liquor bearing the closest resemblance to sulphuric ether. It had the same smell and taste, the same specific gravity, dissolved in 8 or 10. parts of cold water, boiled at the temperature of 100°, dissolved resins and phosphorus, burnt with a white flame leaving a trace of charcoal, but giving no indication of the presence of any acid.

Thus it appears that phosphoric ether approaches very nearly to sulphuric ether, if it be not absolutely the same with it, and differs very considerably from nitric, muriatic, and acetic ethers.

ETHER may be formed also by several other acids. Scheele obtained it by distilling a mixture of fluor spar, black oxide of manganese, alcohol, and sulphuric acid; and Bergman by means of oxalic acid. Scheele found

Chap. IV.

that the following acids did not form ether with alco-Book II. Division II. hol \*, require bandona de ma arme hon , 2 side almond' bias

> 1. Muriatic, 4. Benzoic, 7. Succinic. 2. Fluoric, 5. Tartaric, 8. Arsenic. 3. Boracic, 001 de 6. Citric, administration de baser

> Thus it appears that there are various species of ethers differing very much from each other in their properties. Sulphuric ether is the lightest but the least volatile of the whole. In muriatic and acetic ether an acid seems to enter as a constituent part, but its properties are concealed altogether while the liquid remains undecomposed. It is not unlikely that nitric ether may also contain an acid. It is obvious that the theory of the formation of nitric, muriatic, and acetic ethers must be quite different from that of sulphuric and phosphoric e-The theory of the two last is probably similar. thers.

#### SECT. III. parts of cold water.

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## OF VOLATILE DILS.

The term oil is applied to a number of unctuous liquids, which, when dropt upon paper, sink into it, and make it seem semitransparent, or give it what is called These bodies are very numerous, and a greasy stain. have been in common use from time immemorial. Chemists have divided them into two classes ; namely, volatile and fixed oils. We shall consider the properties of

\* Scheele, ii. 117. Wyd nam grad bear

the first of these classes in this Section. The fixed oils Chap. IV. will occupy our attention in the next. A third class of oils might be added which possess intermediate properties between the fixed and the volatile.

VOLATILE OILS, called also essential oils, are distinguished by the following properties :

1. Liquid; often almost as liquid as water; some- Characters times viscid.

2. Very combustible.

3. An acrid taste and a strong fragrant odour.

4. Volatilized at a temperature not higher than or distilling a kind of resinous hitter called her no. 212

5. Soluble in alcohol, and imperfectly in water.

6. Evaporate without leaving any stain on paper.

By this last test it is easy to discover whether they have been adulterated with any of the fixed oils. Let a drop of the volatile oil fall upon a sheet of writing paper, and then apply a gentle heat to it. If it evaporates without leaving any stain upon the paper, the oil is pure; but if it leaves a stain, it has been contaminated with some fixed oil or other.

Volatile oils are almost all obtained from vegetables, Prepareand they exist in every part of plants; the root, the tion. bark, the wood, the leaves, the flower, and even the fruit, though they are never found in the substance of the cotyledons; whereas the fixed oils, on the contrary, are almost always contained in these bodies \*.

When the volatile oils are contained in great abundance in plants, they are sometimes obtained by simple expression. This is the case with the oil of oranges.

in starter

\* Fourcroy, vii. 352.

of lemons, and of bergamotte; but in general they can only be obtained by distillation. The part of the plant containing the oil is put into a still with a quantity of water, which is distilled off by the application of a moderate heat. The oil comes over along with the water, and swims upon its surface in the receiver. By this process are obtained the oil of peppermint, thyme, lavender, and a great many others, which are prepared and employed by the perfumer. Others are procured by the distillation of resinous bodies. This is the case in particular with oil of turpentine, which is obtained by distilling a kind of resinous juice, called turpentine, that exudes from the juniper.

Properties.

Volatile oils are exceedingly numerous. They have been long known; but as their use in chemistry is but limited, they have not hitherto been subjected to an accurate chemical investigation. They differ greatly in their properties from each other; but it is impossible at present to give a detailed account of each.

Liquidity.

1. The greater number of volatile oils are *liquid*, many indeed are as limpid as water, and have nothing of that appearance which we usually consider as *oily*. This is the case with the following; namely, oil of turpentine, oranges, lemons, bergamotte, roses. Others have the oily viscidity. It varies in them in all degrees. This is the case with the oils of mace, cardomom, sassafras, cloves, cinnamon. Others have the property of becoming solid. This is the case with the oils of parsley, fennel, aniseed, balm. Others crystallize by slow evaporation. This is the case with oil of thyme, peppermint, marjoram. The oil of nutmegs

#### VOLATILE OILS.

has usually the consistence of butter\*. This is the case also with the oil of hops and of pepper.

2. The colour of the volatile oils is as various as Colour. their other properties. A great number are limpid and colourless, as oils of turpentine, avender, rosemary, savine, aniseed. Some are yellow, as spike, bergamotte. Some are brown, as thyme, savony, wormwood. Others blue, as camomile, motherwort. Others green, as milfoil, pepper, hops, parsley, wormwood, cajeput, juniper, sage, valerian. Others, though at first colourless, become yellow or brown by age, as cloves, cinnamon, sassafras †.

3. Their odours are so various as to defy all des-Odour ... cription. It is sufficient to say, that all the fragrance of the vegetable kingdom resides in the volatile oils. Their taste is always acrid, hot, and exceedingly unpleasant. Siles smoond things to bas pains to lio as

4. Their specific gravity varies very considerably, not only in different oils, but even in the same oil in different circumstances. The following are the specific gravities of several of the volatile oils, as ascertained by Dr Lewis t. the same

Oil

The bidge of

l of sassafras 1.094	Oil of Mint 975
Cinnamon 1.035	Nutmegs 948
Cloves1.034	tansy946
Fennel 997	Carraway seeds 940
Dill 994	Origanum 940
Penny royal 978	Spike936
Cummin 975	Rosemary 934

\* Fourcroy, vii. 505. Eng. Trans. + Neuman's Chem. p. 272. ! Ibid. a Margueron Aver de Pere rie 136.

Specificgra vity.

TYPETT DATA

Chap. IV.

Volatific

Book II. Division II. Volatility.

When the volatile oils are heated in the open air, they evaporate readily, and without alteration, diffusing their peculiar odours all around; but there is a considerable difference between the different oils in this respect. When distilled in close vessels, they do not so readily assume the form of vapour. Hence they lose their odour, become darker in colour, and are partly decomposed. Oils do not seem very susceptible of assuming the gaseous form, unless some other substance, as water, be present.

When exposed to the action of cold, they congeal like the fixed oils; but the temperature necessary to produce this effect varies according to the oil. Some of them, as oil of anise and of fennel, become solid at the temperature of  $50^\circ$ : frozen oil of bergamotte and of canella become liquid at  $23^\circ$ ; oil of turpentine at  $14^\circ$ <sup>\*</sup>. Margueron exposed several volatile oils to a cold of  $-17^\circ$ . They congealed or rather crystallized partially, and at the same time emitted an elastic fluid. These crystals consisted partly of the oils themselves, partly of other substances. Some of them had the properties of benzoic acid  $\dagger$ .

Changed by light. 6. Volatile oils, when exposed to the action of light in close vessels, and excluded from common air, undergo very singular changes. Their colour becomes deeper, they acquire a great deal of consistency, and their specific gravity is considerably increased. The cause of

\* Margueron, Jour. de Phys. xlv. 136. +1

+ Ibid.

#### VOLATILE OILS.

these changes is but imperfectly known. Tingry, to whom we are indebted for these interesting researches. has proved that light is a necessary agent. It was supposed formerly that they were occasioned by the absorption of oxygen; and when oxygen is present, it has been ascertained that it is absorbed : but Tingry has proved that the same changes go on when oxygen is excluded. This philosopher ascribes them to the fixation of light. If this be the real cause, the quantity of light fixed must be enormous; for as the specific gravity of the oils is increased considerably while the bulk continues the same, it is evident that the absolute weight must be increased proportionably. One circumstance, however, renders this conclusion somewhat doubtful, at least in its full extent; and that is, that the quantity of change was always proportional to the quantity of the oil and the quantity of air contained in the vessel \*.

7. When volatile oils are exposed to the open air, they Absorb gradually become deeper coloured, and acquire more and more viscidity, while at the same time their odour diminishes. Dr Priestley first ascertained that they imbibe oxygen with rapidity, and that the changes are owing to this absorption. He tried the experiment only with oil of turpentine, but he found that the air above oils of mint and cinnamon, confined in phials half full, was deprived of its oxygen +. He ascertained likewise, that, independent of this disposition to absorb oxygen, oil of turpentine has the property of imbibing a consi-

> \* Tingry, Jour. de Phys. 11vi. 161, and 249. + Priestley on Air, ii 232. Hh

Vol. II.

oxygen,

derable quantity of air, which may be afterwards extricated by means of the air-pump  $\ddagger$ . According to Fourcroy, this absorption of oxygen is accompanied by the formation of water. His evidence for this is, that drops of water, he says, are often perceptible at the *surface* of those oils that are kept in vessels not properly closed §. By long exposure the volatile oils assume the form of resins.

When the volatile oils are heated sufficiently in the open air, they take fire and burn with a clear bright flame, emitting a vast quantity of smoke. The products of the combustion, besides the soot, are water and carbonic acid.

5. When agitated with water, the greater number of the volatile oils render it milky, and communicate to it their peculiar odour. Several of them when dropt upon sugar, if the sugar be afterwards dissolved in water, form a permanent solution, to which the name of *oleo*saccharum has been given. Margueron has shown that this property belongs only to the purest and most limpid part of the oils.

Action of alcohol, ether, fixed oils.

Oleo-sac-

charum.

Action of simple combustibles,

They are all soluble in alcohol, ether, and fixed oils; though they vary considerably in the facility with which they unite to alcohol. Oil of turpentine, for instance, is known to unite slowly with that liquid. When one part of that oil is dissolved in seven parts of alcohol, the oil separates by degrees, and sinks to the bottom \*.

9. The action of the simple combustibles upon the volatile oils is not remarkable. They do not absorb

- † Priestley on Air, ii. 232.
- § Fourcroy, vii. p. 501. Eng. Trans.
- \* Neuman's Ghem. p. 288.

#### VOLATILE OILS.

hydrogen as far as is known, neither are they altered Chap. IV. by charcoal. When digested upon sulphur at the temperature at which the sulphur melts, they dissolve a portion of it, acquire a brown colour, and a disagreeable taste and smell. These preparations are called balsams of sulphur. A portion of the sulphur crystallizes as they cool \*. When these balsams are heated strongly, a vast quantity of gas (probably sulphureted hydrogen) is evolved so rapidly as to occasion very violent explosions, unless proper precautions be taken +.

The volatile oils dissolve likewise a portion of phosphorus in a digesting heat; but most of them deposite the whole of it again as the solution cools. Hoffman pointed out a method of rendering the solution permanent. It was the following: Triturate together ten parts of camphor and one of phosphorus. This mixture dissolves readily in most volatile oils, as in oil of cloves, and forms a solution which has the property of rendering every thing luminous which is rubbed with it, and this without combustion 1. This seems to have been the solution so much used by Boyle, under the name of liquid phosphorus.

10. The alkalies and earths act but feebly upon the volatile oils. The French chemists have proposed to give the combinations which these bodies form with the volatile oils the name of savonules, which Dr Pear-

Of alkalies and earths,

\* Elemens de Chymie of the Dijon Academy, iii. 357.

+ Hoffman relates a remarkable story of the violent effects of such an explosion by way of caution to the chemists of his time, - Observationes Phys. Chem. p. 308.

Hoffman, Observ. Phys. Chem. F. 307.

Hh2

Book II. Division II. son has translated by the term *saponules* ; but these denominations have not been adopted by chemists \*.

Whoever considers the tedious trituration of potash and oil of turpentine together, by which the medicinal preparation called Starkey's soup is prepared, and compares it with the facility with which that alkali dissolves common turpentine, will be inclined to believe that the combination takes place only in so far as the oil is converted into a resin; and that it is not the oil which has the property of uniting with potash, but the resin formed by its absorbing oxygen from the atmosphere. Indeed it is not improbable, that the volatile oils absorb, and part with oxygen, with much greater facility than has been hitherto supposed; and that during many of their solutions these changes take place. Volatile oils seem to unite to alkalies and earths only when united to oxygen so as to form resins; while resins, on the other hand, may probably owe their solubility in alcohol to their parting with oxygen, and assuming the state of volatile oils. Some recent experiments of Mr Hatchett at least render the last supposition not improbable. I shall mention one: He took about half a pound of the common yellow resin of the shops, and having dissolyed it in rather less than a quart of alcohol, he poured the clear solution from the dregs and impurities into a glass basin containing about two quarts of distilled water. He placed this basin on a sand bath, and heated it moderately for about four hours. The principal part of the resin was precipitated during this digestion.

\* The term saponule does not agree well with the idiom of our language. The word subscop, or something similar, would have been better.

#### VOLATILE OILS.

Next day the milky liquor was poured off the precipitate, and evaporated to dryness in an open vessel. During the evaporation, brittle films of perfect resin were formed successively on the surface of the liquor, and the dry residue, after evaporation, was likewise complete resin; but the portion which had precipitated in the first basin, and which constituted the chief part of the original, was not in the state of resin, but of common turpentine. These phenomena indicate in a very unequivocal manner, that oxygen had been taken from the resin during its solution in alcohol. Hence the portion which precipitated immediately when the solution was poured into water, not being in contact with the air, fell down in the state of turpentine; while the portion that continued in contact with air became perfect resin.

11. The action of the acids upon the volatile oils has Of acide. been but imperfectly examined.

Sulphuric acid acts upon them with considerable energy : dissolving them, converting them at first to a substance of a resinous nature, and at last reducing them to the state of charcoal. Hence we may procure the oil in very different states, by separating it from the acid at the end of a longer or shorter interval by pouring the mixture into water. When a volatile oil is dropt very slowly into four times its weight of sulphuric acid, triturating constantly after every addition, a solution is formed of a brownish colour. If this solution is poured into three or four parts of water, and then gently heated, a brown mass separates, which was formerly known by the name of an acid soap. Achard is the only chemist who has examined these combinations with attention. His experiments were made chiefly on oil

Chap. IV.

of turpentine. The mass which separates when this oil and sulphuric acid are treated as above described, is of the consistence of soft wax, soluble in water and alcohol; and when decomposed by an alkali, the oily matter which separates unites readily with alkalies \*. Hence it appears that it has approached the state of a resin.

Muriatic acid has much less action on them than the sulphuric. From Achard's trials it dissolved  $\frac{1}{120}$ th of its weight of the oil of sassafras. The portion dissolved is probably altered +.

When nitric acid is thrown upon them suddenly, and in a concentrated state, it acts with such energy as to set them on fire; but when sufficiently diluted with water it dissolves them, and converts them into a yellow substance similar to resin. Oxymuriatic acid acts in the same way, though with less energy.

12. The action of the volatile oils on metals has not been examined with care, but it cannot be remarkable. Margueron has tried the effect of some of the salts of mercury upon several volatile oils. The following are the facts ascertained by this chemist: When oil of rosemary is kept over nitrate of mercury, the salt is gradually decomposed, and the oil acquires a deep colour. Oxymuriate of mercury, in like manner, deepens the colour and increases the consistence of oils of citron, chevril, hysop, lavender, rosemary, and peppermint; while it is at the same time partly converted into muriate of mercury. Neither the muriate of mercury, nor

\* Jour. de Phys. xvi. 409.

Elemens de Chymie of the Dijon Academy, iii. 361.

#### VOLATILE OILS.

the sulphuret of that metal, produce any change in the oils of lavender and rosemary; but by this last oil the red oxide of mercury is converted into the black, though the oil does not experience any sensible change. The oxymuriate of antimony is likewise decomposed by the oil of rosemary \*.

13. From the effects of the acid supporters on the volatile oils, and from the products which they yield when burnt, it has been concluded that they are composed of hydrogen and carbon, sometimes united with various proportions of oxygen according to circumstances: but no exact analysis has yet been made of any of them.

14. Volatile oils are applied to a great number of uses: Some of them are employed in medicine; some of them, as oil of turpentine, are much used to dissolve resins, which are afterwards employed as varnishes. Not to mention their employment in painting and in perfumery.

## SECT. IV.

#### OF FIXED OILS.

THE fixed oils, which are of such extensive utility in Discovery. the arts, were known at a very remote period. They are mentioned in Genesis, and during the time of Abraham were even used in lamps +. The olive was very early cultivated, and oil extracted from it, in Egypt.

# Ann. de Chim. xlvii. 66.

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+ Gen. xv. 17.

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Cecrops brought it from Sais, a town in Lower Egypt, where it had been cultivated from time immemorial, and taught the Athenians to extract oil from it. In this manner the use of oil became known in Europe\*. But the Greeks seem to have been ignorant of the method of procuring light by means of lamps till after the siege of Troy; at least Homer never mentions them, and constantly describes his heroes as lighted by torches of wood.

FIXED OILS are distinguished by the following characters :

Characters.

1. Liquid, or easily become so when exposed to a gentle heat.

- 2. An unctuous feel.
- 3. Very combustible.
- 4. A mild taste.
- 5. Boiling point not under 600°.
- 6. Insoluble in water and alcohol,

7. Leave a greasy stain upon paper.

## Prepara-

These oils, which are also called *fat* or *expressed* oils, are numerous, and are obtained, partly from animals and partly from vegetables, by simple expression. As instances, may be mentioned whale oil or train oil, obtained from the blubber of the whale and from cod; olive oil, obtained from the fruit of the olive; linseed oil and almond oil, obtained from linseed and almond kernels. Fixed oils may also be extracted from poppy-seeds, hempseeds, beech-mast, and many other vegetable substances.

It deserves attention, that the only part of vegetables in which fixed oils are found is the seeds of bicotyledi-

# Herodot. lib. ii. 59. and 62.

nous plants\*. In animals they are most usually deposited in the liver, though they are found also in the eggs of fowls.

All these oils differ from each other in several particulars, but they also possess many particulars in common. Whether the oily principle in all the fixed oils is the same, and whether they owe their differences to accidental ingredients, is not yet completely ascertained, as no proper analysis has hitherto been made; but it is not improbable, as all the oils hitherto tried have been found to yield the same products. In the present state of our knowledge, it would be useless to give a particular description of all the fixed oils, as even the differences between them have not been accurately ascertained.

1. Fixed oil is usually a liquid with a certain degree Properties. of viscidity, adhering to the sides of the glass vessels in which it is contained, and forming streaks. It is never perfectly transparent, having always a certain degree of colour; most usually it is yellowish or greenish. Its taste is sweet, or nearly insipid. When fresh it has little or no smell.

There exist also in the vegetable kingdom a considerable number of bodies, which at the ordinary temperature of the atmosphere are solid, and have hitherto been considered as fixed oils. Palm oil may be mentioned as an example, which has been lately subjected to a chemical examination by Dr Bostock †. The various substances used in India and Africa as substitutes for butter, and as unguents, may likewise be mentioned.

\* Fourcroy, vii. 319.

+ Nicholson's Journal, xvi. 161.

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Most of them are obtained from the seeds of trees; different species of the *bassia*, as the *butyracea*, *longifolia*, *latifolia*, *obovata*, yield this butyraceous matter. They have been described by Dr Roxburgh §. The shea or butter tree of Africa described by Park, seems also to be a species of bassia. These substances, from the experiments of Dr Bostock, appear to differ a little from the liquid fixed oils in their properties, and to approach the nature of wax. Thus they are sensibly soluble in alcohol and ether, and do not combine so readily with alkalies as the fixed oils.

Specific gravity. 2. All the fixed oils hitherto examined are lighter than water; but they differ greatly from one another in specific gravity. The same difference is observable in different samples of the same oil. The following Table contains the specific gravity of such oils as have been examined.

> Oil of palm \* ....968 Hazel-nuts\* 941 Poppies\* ..939 Linseed † ..932 Almonds\* 932 Walnuts\*..923 to 947 Beech-nut\* 923 Ben\* .....917 Olives† ..913 Rape-seed† 913 Cacao‡ .. 892

Pola .

Action of heat.

3. Fixed oil does not begin to evaporate till it be

† Brisson.

- § Nicholson's Jour. xix. 372.
- \* Fabroni, Crell's Annals, 1797, ii. 123.
- + Shaw's Boyle, ii. 346.

#### FIXED OILS.

heated above the boiling point of water. As the heat Chap. V. increases, a pretty copious vapour may be seen rising from it; but the oil does not begin to boil till it is heated nearly up to the temperature of 600°. At that temperature it may be distilled over; but it is always. somewhat altered by the process. Some water and, acetic acid seem to be formed, a little charcoal remains, in the retort, and the oil obtained is lighter, more fluid, and has a stronger taste than before. Oil, thus distilled, was formerly distinguished by the name of philosophical oil. During the distillation, a great quantity of heavy inflammable air is obtained.

Fixed oil, when in the state of vapour, takes fire on the approach of an ignited body, and burns with a yellowish white flame. It is upon this principle that candles and lamps burn. The tallow or oil is first converted into the state of vapour in the wick; it then takes fire, and supplies a sufficient quantity of heat to convert more oil into vapour; and this process goes on while any oil remains. The wick is necessary to present a sufficiently small quantity of oil at once for the heat to act upon. If the heat were sufficiently great to keep the whole oil at the temperature of 600°, no wick would be necessary, as is obvious from oil catching fire spontaneously when it has been raised to that temperature. When oil is burnt in this manner, either in the open air or in contact with oxygen gas, the only new products obtained are water and carbonic acid.

When exposed to the action of cold, fixed oils lose their fluidity, and are converted into ice; but this change varies exceedingly in different oils.

3. When fixed oils are exposed to the open air or to Action of oxygen gas, they undergo different changes according to air.

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whit of

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the nature of the oil. All of them, as far as experiment has gone, have the property of absorbing oxygen; and by uniting with it they become more and more viscid, and terminate at last in a solid state, being apparently saturated with oxygen. Now there are some oils that retain their transparency after they have become solid; while others become opaque, and assume the appearance of *tallow* or *wax*. This circumstance has given occasion to the division of the fixed oils into two classes: Those that remain transparent are called *drying oils*, while those that become opaque are called *fat oils*.

Drying oils.

4. The drying oils are used as the vehicle of paints and varnishes. Linseed, nut, poppy, and hemp-seed oils, belong to this class. These oils in their natural state possess the property of drying oils but imperfectly. To prepare them for the use of the painter and varnish maker, they are boiled for some time in an iron pot. By this process they are partly decomposed; abundance of watery vapour and of carbureted hydrogen gas is separated from them. They become deeper coloured. and acquire greater consistency. It is common for some purposes to set them on fire, to allow them to burn for some time, to extinguish them by covering up the vessel in which they are contained, and to continue the boiling till they acquire the proper degree of viscidity. By this process they lose their unctuous quality in a great measure, so as not to leave a greasy stain upon paper, and approach the nature of resins, with this difference, that they do not become brittle, but retain a degree of toughness and ductility, not unlike what in this country is called wrought rosin, or shoemaker's rosin. It is common also in preparing the drying oils to

boil them with a little litharge. The change which happens to the oils by this process has not been precisely ascertained. Probably they absorb oxygen from the air, and we know that they undergo a partial decomposition. When they burn for some time, their unctuous quality is much more completely destroyed than by any method which has yet been practised. Hence it is followed frequently in preparing the drying oils for varnishes, and always for printers ink, which requires to be as free as possible from all unctuosity.

Nut oil has been found preferable to all other oils for printers ink ; though the dark colour which it acquires during boiling renders it not so proper for red ink as for black. Linseed oil is considered as next after nutoil in this respect. Other oils cannot be employed, because they cannot be sufficiently freed from their unctuosity. Ink made with them would be apt to come off and smear the paper while in the hands of the book-binder, or even to spread beyond the mark of the types, and stain the paper yellow. The process for making printers ink is as follows:

The oil is made to boil in an iron pot only half Printers filled, set on fire, and allowed to burn for half an hour or more, then boiled gently till it acquires the proper consistence. In this state it is called the varnish. Two kinds are prepared, a thicker and a thinner. ' The thicker is of such a consistence that it draws into threads when cold like weak glue. This varnish is afterwards ground with lamp-black in the proportion of two ounces and a half to sixteen ounces of oil. When newly prepared oil is used for making ink, it is said to be necessary to add a little boiled oil of turpentine and a little

ink.

Chap. IV.

Book II. Division II. litharge; but this is said to have the effect of causing the ink to stick so firmly to the types, that it can with difficulty be removed. Old oil does not require this addition \*.

Oil prepared by the process above described, is still insoluble in alcohol and water, but it unites readily to more oil. It dries into a tough mass like turpentine, and afterwards is scarcely susceptible of uniting with oil. Dr Lewis found that linseed oil, when thus converted into a thick varnish, lost  $\frac{1}{6}$ th of its weight; when boiled till it became quite stiff when cold, it lost nearly  $\frac{1}{2}$ of its weight<sup>+</sup>. The property which printers ink has of adhering to moistened paper shows that the oily nature of the body is greatly altered. In some respects it has approached the nature of mucilage, though in others the difference is very great.

Fat oils.

5. The *fat oils*, when exposed to the atmosphere, gradually become thick, opaque, and white, and assume an appearance very much resembling wax or tallow. Olive oil, oil of sweet almonds, of rape-seed, and of ben, belong to this class.

When oil is poured upon water, so as to form a thin layer on its surface, and is in that manner exposed to the atmosphere, these changes are produced much sooner. Berthollet, who first examined these phenomena with attention, ascribed them to the action of light: but Sennebier observed that no such change was produced on the oil though ever so long exposed to the light, provided atmospherical air was excluded; but that it took place on the admission of oxygen gas, whether the

\* Lewis, Fhil. Com. p. 371.

+ Ibid. 372.

oil was exposed to the light or not\*. It cannot be Chap. IV. doubted, then, that it is owing to the action of oxygen. It is supposed at present to be the consequence of the simple absorption of oxygen and its combination with the fat oils.

6. The action of fixed oils upon the simple combustibles is not very remarkable.

Hydrogen, as far as known, does not act upon them. When they are filtered through charcoal powder, they are rendered purer; but on account of the great difficulty of separating the charcoal from fixed oils, it cannot be employed with advantage for purifying them t. Black paint is usually nothing else than charcoal in some state or other ground up with a drying oil.

The fixed oils likewise dissolve a small proportion of phosphorus when assisted by heat. The combination succeeds easiest if a mixture of oil, water, and phosphorus be boiled for a little in a glass vessel. These oily phosphurets emit the odour of phosphureted hydrogen, and yield, when distilled, a portion of that gas. When rubbed in the open air, or when spread upon the surface of other bodies, they appear luminous, in consequence of the combustion of the phosphorus. When hot oils saturated with phosphorus are allowed to cool, the phosphorus crystallizes in octahedrons, as Pelletier ascertained.

They readily dissolve sulphur when assisted by heat. The solution assumes a reddish colour. When distilled, there comes over a great quantity of sulphureted hy-

> \* Ann. de Chim. xi. 89. + Kels, Crell's Annals, iii. 274. Engl. Trans.

Action of simple combustibles,

#### COMPOUND COMBUSTIBLES.

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Of water.

drogen gas. When the solution is allowed to cool, the sulphur is deposited in crystals. By this process Pelletier obtained sulphur in regular octahedrons.

7. The fixed oils are all insoluble in water. When agitated with that liquid, the mixture becomes milky, but the oily particles gradually separate and swim upon the surface. The presence of a mucilaginous substance, as gum arabic, prevents the oil from separating, and occasions, of course, a permanent milkiness. Such mixtures are called *emulsions*. They are often formed by triturating oily seeds, as almonds, with water; the two ingredients necessary to form an emulsion, oil and mucilage, being present in the seed.

Alcohol,

Ether.

Alkalies.

12

The fixed oils are insoluble in alcohol. They continue insoluble in it even after being thickened by boiling; but if they be united to an alkali, and afterwards separated by an acid, they will be found to have acquired the property of dissolving in alcohol: a proof that the oil has undergone an alteration in its composition by being united to an alkali\*.

The fixed oils are also insoluble in ether; but they unite readily with each other, with volatile oils, and likewise with bituminous and resinous substances.

8. The alkalies unite readily with the fixed oils, and form the important compounds called *soaps*. The fat oils enter into these combinations more readily than the drying oils. The earths likewise combine with these oily bodies, and form a kind of soap insoluble in water, and therefore not capable of being applied to the same uses as common soap.

\* Elemens de Chymie of the Dijon Academy, iii. 400.

9. The combustible acids, as far as is known at present, do not unite with oils; neither has the muriatic Acids; acid any remarkable effect. Phosphoric acid, when concentrated, deepens their colour, and gives them a peculiar smell, especially if assisted by heat: a proof that it acts upon them \*. The sulphuric acid acts with much greater energy. The oils become immediately black, and assume gradually the properties of bitumen in proportion to the continuance of the action. If the acid be allowed to remain long enough, they are completely decomposed; water is formed, charcoal precipitated, and an acid evolved +. Other products doubtless also make their appearance, though the action of this acid on oils has not yet been examined with sufficient care. Nitric acid acts with still greater energy. When poured suddenly upon the drying oils, it sets them on fire. The same effect is produced upon the fat oils, provided the acid be mixed previously with a portion of the sulphuric. When the nitric acid is sufficiently diluted, it converts the drying oils into a yellow resinous-like mass, and the fat oils to a substance very like tallow. But the action of this acid upon fixed oils has not yet been sufficiently examined.

Many attempts have been made by chemists to form Acid soaps. permanent compounds of the concentrated acids and oils under the name of acid soaps. The only acid which was found to answer was the sulphuric. Achard published a number of experiments on these compounds. They dissolve in water, and lather like common soap;

\* Elemens de Chemie of the Dijon Academy, iii. 142. † Fourcroy, vii. 330.

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Action on metals, but as they are not in reality permanent compounds, they cannot be used with much prospect of advantage.

10. The fixed oils act (though feebly) upon some of the metals when the atmospheric air is not excluded. Copper is soon corroded by them, and a dark green solution obtained. The only other metal upon which they are known to act in the same manner is mercury. By triturating mercury with fixed oils, it gradually disappears, and a bluish coloured unguent is formed; consisting, in part at least, of the black oxide of that metal united to the oil. But this experiment scarcely succeeds except with those oils which are in a state approaching to solidity.

But upon the metallic oxides the fixed oils act with greater energy. They dissolve the white oxide of arsenic with great facility, as was shown long ago by Brandt. When boiled with the oxides of mercury, lead, or bismuth, they form very tough solid compounds, called *plasters*.

Rancidity.

11. Fixed oils are liable, by keeping, to undergo a change well known by the name of *rancidity*. They become thick, acquire a brown colour, an acrid taste, and a disagreeable smell. The oil thus altered converts vegetable blues into red, and of course contains an acid. It is believed at present that this change is owing to the alteration of the foreign substances present in oils, or to the action of those foreign bodies upon the oily matter itself. Several of the fixed oils, when newly extracted, let fall on standing a quantity of mucilaginous matter; and from the experiments of Scheele, it appears probable that they always retain less or more of a similar principle. He boiled together one part of litharge, two parts of olive oil, and a little water.

When the oil had acquired the consistence of an oint- Chap. IV. ment, it was allowed to cool, and the water decanted off. When this water is evaporated to the consistence of a Sweet pri syrup, it leaves a substance which Scheele termed the sweet principle of oils. It does not crystallize, is soluble in water and alcohol, and is converted into oxalic acid by the action of nitric acid. When heated, it is partly decomposed into a brown oil, and partly volatilized unaltered. This substance he obtained also from linseed and rape-seed oil, and from oil of almonds. Even the oil disengaged from soap yielded him a little of it \*. Similar impurities were supposed to exist in all fixed oils, and to occasion their rancidity by putrefaction. This rancidity is in some degree diminished by agitation with water, but not completely destroyed. Mr Dossie has shown that agitation with the fixed alkaline solutions and quicklime answers the purpose sufficiently well in purifying oils for burning in lamps; but that they have the property of coagulating a portion of the This however may be prevented by adding a oil. quantity of strong brine, which occasions the separation of the foreign bodies from the oil +.

12. When oil is burnt, the only products arec arbonic Composiacid and water. When repeatedly distilled, or when passed through a red hot tube, it appears to be completely converted into water, carbonic acid, and heavy inflammable air. Lavoisier analysed olive oil by burning it in a vessel filled with oxygen gas. During the combustion there was consumed

tion of oils.

ciple of oi

# Scheele's Opusc. ii. 189.

+ Nicholson's Jour. v. C. II 2 III

#### COMPOUND COMBUSTIBLES.

Book II. Division II. Of oil.....15.79 grains troy Of oxygen gas.....50.86

When the water

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The products were carbonic acid and water. The carbonic acid obtained amounted to 44.50 grains: the weight of the water could not be accurately ascertained; but as the whole of the substances consumed were converted into carbonic acid gas and water, it is evident, that if the weight of the carbonic acid be subtracted from the weight of these substances, there must remain precisely the weight of the water. Mr Lavoisier accordingly concluded by calculation, that the weight of the water was 22.15 grains. Now the quantity of oxygen in 44.50 grains of carbonic acid gas is 32.04 grains, and the oxygen in 22.15 grains of water is 18.82 grains; both of which taken together amount to 50.86 grains, precisely the weight of the oxygen gas employed.

The quantity of charcoal in 44.50 grains of carbonic acid gas is 12.47 grains; and the quantity of hydrogen in 22.15 grains of water is 3.32 grains; both of which, when taken together, amount to 15.79 grains, which is the weight of the oil consumed.

It follows, therefore, from this analysis, that 15.79 grains of oil are composed of 12.47 carbon

3 32 hydrogen

Olive oil therefore is composed of about

79 carbon 21 hydrogen 100\*

\* Mem. Par. 1784, and Jour. de Phys. for 1787, July.

# FIXED OILS.

This, however, can only be considered as a very imperfect approximation towards the truth. The fixed oils no doubt vary in the proportion of their constituents; and the phenomena of their decomposition lead us to conclude, that many of them contain oxygen as a component part \*.

BESIDES the volatile and fixed oils, there is another set which exist pretty frequently in the vegetable kingdom. Their chemical properties are intermediate between the fixed and the volatile oils. Like the volatile oils they dissolve in alcohol; but like the fixed they cannot be distilled over with that liquid. Hence they may be obtained by digesting the vegetable substance that contains them in alcohol, and then separating the alcohol from the oil by distillation. They have all a strong acrid taste, and most of them possess poisonous qualities. The alcoholic solution of some of them has the property of precipitating sulphate of iron of a reddish colour, which becomes green when mixed with an alkaline solution. Vauquelin detected an oil of this nature in the root of the helleborus hyemalis +. A similar oil appears to exist in tobacco and in many other plants.

\* Besides the oils which exist ready formed in the vegetable and animal kingdom, there are a variety of others which are obtained when animal or vegetable bodies are distilled by means of a heat above that of boiling water. These oils have received the appellation of *empyreumatic*, because they are formed by the action of fire. They have never been examined with attention; but most of them seem to possess the properties of the volatile oils. Their odour is always exceedingly disagreeable, and their taste acrid.

† Ann. de Mus. d'Hist. Nat. No. xliji. 82.

Poisonous oils.

Division

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# SECT. IV. nodedy wit bas sates

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#### OF BITUMENS.

THE term bitumen has often been applied by chemists to all the inflammable substances that occur in the earth ; but this use of the word is now so far limited, that sulphur and mellite are most commonly excluded. It would be proper to exclude amber likewise, and to apply the term to those fossil bodies only which have a certain resemblance to oily and resinous substances. In this restricted sense the word is used in the present Section.

Division.

Bituminous substances may be subdivided into two classes; namely, bituminous oils, and bitumens, properly so called. The first set possess nearly the properties of volatile oils, and ought in strict propriety to be classed with these bodies; but as the chemical properties of bitumens have not yet been investigated with much precision, it was deemed rather premature to separate them from each other. The second set possess properties peculiar to themselves. Let us endeavour to describe the substances belonging to these two classes as far as possible.

# I. BITUMINOUS OILS.

La contration areas

ONLY two species of bituminous oils have been hitherto examined by chemists. Others indeed have been

#### BITUMENS.

mentioned, but their existence has not been sufficiently authenticated. These two species are called petroleum, II m and maltha or sea-wax; the first is liquid, the second solid.

1. Petroleum is an oil of a brownish yellow colour. Petroleum. When pure, it is fluid as water, and very volatile \*. Its specific gravity varies from 0.730 to 0.878 +. It has a peculiar smell. When heated, it may be distilled over without alteration. It unites with alcohol, ether, volatile and fixed oils, and, as far as known, possesses all the characters of volatile oils.

Petroleum is found in the earth in various states of purity; sometimes without any mixture of foreign substances. In this state it is usually distinguished by the name of naphtha, and is said to occur in great abundance on the shores of the Caspian and in Persia. It occurs also in different parts of Europe, especially Italy and Germany. When less fluid and darker coloured, it is commonly called petroleum. It is supposed to owe this increased spissitude and deepened colour to the action of the air. When distilled, it yields a quantity of pure petroleum, while a portion of bitumen of the consistence of tar or pitch remains behind. When long exposed to the air, petroleum becomes black, and acquires the semifluidity of tar. In this state the greatest part of it is insoluble in alcohol; so that it has assumed the state of true bitumen.

\* The volatility seems to have been over-rated by older chemical writers. On mixing well rectified petroleum with water in a retort, I found that the water could be readily distilled over in a moderate heat, while the whole petroleum remained behind.

+ See Kirwan's Mineralogy, ii. 42.

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Sea-wax.

Petroleum is used in those countries where it abounds as an oil for lamps. It is employed also as a solvent of resinous bodies, and of the proper bitumens, which it dissolves with facility.

4. Sea-wax, or maltha, is a solid substance found on the Baikal lake in Siberia. It is white, melts when heated, and on cooling assumes the consistence of white cerate. It dissolves readily in alcohol, and in other respects appears to possess the characters of a solid volatile oil. Its properties, however, have been but imperfectly examined. Klaproth found that a similar substance was obtained by distilling a species of wood coal, called earth coal by the Germans \*.

Mineraltallow The substance described by Kirwan under the name of mineral tallow, and said to have been found on the coast of Finland, in the Swedish lakes, and in a fountain near Strasburgh, seems to approach very nearly to sea-wax. Its specific gravity is 0.770. It is while, brittle, stains paper like oil, melts when heated, and burns with a blue flame and much smoke; dissolves imperfectly in hot alcohol, but readily in olive oil  $\dagger$ .

# II. PROPER BITUMENS.

THE true bituminous substances may be distinguished by the following properties :

Characters.

1. They are either solid or of the consistence of tar.

- 2. Their colour is usually brown or black.
- 3. They have a peculiar smell, or at least acquire

\* Beitrage, iii. 325.

+ Kirwan's Mineralogy, ii. 47.

This smell is known by the name of Chap. IV. it when rubbed. the bituminous odour.

4. They become electric by friction, though not insulated t.

5. They melt when heated, and burn with a strong smell, a bright flame, and much smoke.

6. They are insoluble in water and alcohol, but dissolve most commonly in ether, and in the fixed and volatile oils.

7. They do not dissolve in alkaline leys, nor form soap.

8. Acids have little action on them; the sulphuric scarcely any : the nitric, by long and repeated digestion, dissolves them, and converts them into a yellow substance, soluble both in water and alcohol, and similar to the product formed by the action of nitric acid on resins 1.

The bitumens at present known may be reduced to three; namely, asphaltum, mineral tar, and mineral Bitumen has been found also united to a caoutchouc. resinous compound, in a curious substance first accurately examined by Mr Hatchett, to which he has given the name of retinasphaltum. United to charcoal in yarious proportions, it constitutes the numerous varieties of pit-coal, so much employed in this country as fuel.

1. Asphaltum. This substance occurs in great a- Asphaltum. bundance in different countries, especially in the island of Trinidad, on the shores of the Dead Sea, and in Albania, where it is found in vast strata. It is supposed

† Hauy.

t Hatchett.

i ropertica:

Book II. Division II.

I. that it was first liquid, and that it acquired solidity J. by exposure to the air.

Its colour is black, with a shade of brown, red, or grey. Its specific gravity varies. That of Albania, as ascertained by Klaproth, was 1.205 \*; but it was somewhat contaminated with earth. Kirwan, in purer specimens, found the specific gravity to vary from 1.07 to 1.165 +. Klaproth has lately published an analysis of the asphaltum of Albania.

Properties.

He found it insoluble both in acids and alkalies, as also in water and alcohol; but soluble in oils, petroleum, and sulphuric ether. Five parts of rectified petroleum dissolved one part of asphaltum without the assistance of heat, and formed a blackish brown solution, which by gentle evaporation left the asphaltum in the state of a black brown shining varnish. The solution in ether was of a pale brown red colour; and when evaporated, the asphaltum remained in the state of a semifluid substance of a reddish colour, still insoluble in alcohol.

Action of heat. A hundred grains of this asphaltum being distilled in a retort, by a heat gradually raised to redness, yielded the following products:

36 cubic inches (German) of heavy inflammable air, 16
A light brown fluid oil
Water slightly tainted with ammonia 6
Charcoal 30
Ashes

100

\* Beitrage, it'. 315.

+ Mineralogy, il. 46.

# BITUMENS.

These ashes consisted chiefly of silica and alumina, with Chap. IV. some iron, lime, and manganese \*.

The asphaltum found in Albania is supposed to have Uses. constituted the chief ingredient of the Greek fire. The Egyptians are said to have employed this bitumen in embalming. It was called mumia mineralis t. The ancients inform us that it was used instead of mortar in building the walls of Babylon.

2. Asphaltum is seldom absolutely pure; for when alcohol is digested on it, the colour of the liquid becomes yellow, and by gentle evaporation a portion of petroleum is separated 1. Mineral tar seems to be Mineral tar. nothing else than asphaltum containing a still greater proportion of petroleum. When alcohol is digested on it, a considerable quantity of that oil is taken up; but there remains a black fluid substance like melted pitch, not acted upon by alcohol, and which therefore appears to possess the properties of asphaltum, with the exception of not being solid §. By exposure to the air, it is said to assume gradually the state of asphaltum.

3. Mineral caoutchouc is a singular substance, hither- Mineral cato found only in Derbyshire. It is soft and very elastic, not unlike common caoutchouc, or Indian rubber, and, like that substance, it may be employed to efface pen-

Action & and One Munified to a of this a in a report gradually raised to a rod heat, wielded the

+ Watson's Chem. Essays, iii. 4. \* Klaproth's Beitrage, iii. 316. t Hatchett's Observations on the Change of some of the Principles of Vegetables into Bitumen. Pbil. Trans. 1804.

§ Chemists and mineralogists have united mineral tar to petroleum as a variety. If it be true that pure petroleum is insoluble in alcohol, that arrangement is right; but I suspect a mistake. I had no opportunity of trying naphtha; but the putest petroleum I have been able to procure readily yields to alcohol, unless it has been left exposed to the air.

outchouc.

#### COMPOUND COMBUSTIBLES.

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cil marks from paper; but it soils the paper a little. Its colour is dark brown, sometimes with a shade of green, at other times of red. The first account of it was published by Dr Lister in the Philosophical Transactions for 1673 \*. It occured in an old forsaken mine in Derbyshire. He calls it a subterraneous fungus, and is uncertain whether it belongs to the vegetable or mineral kingdoms; but rather inclines to the former opinion, and hints that it may have grown out of the old birch props used in the mine. It was first accurately described by Mr Hatchett. Delametherie first examined its properties; and an analysis of it has been lately published by Mr Klaproth.

Properties.

According to Klaproth, it resists the action of almost all liquid menstrua; neither alcohol, alkalies, nor nitric acid affecting it. Even oils were not found by him to dissolve it, though Delametherie assures us that he obtained a solution of it in olive oil +. Petroleum succeeded best with Klaproth, assuming a bright yellow colour, while the caoutchouc was rendered transparent 1. When heated it melts, takes fire, and burns with a bright flame and a bituminous smell. The melted mass still continues adhesive, and may be drawn out into threads. It is now soluble in oils §.

Action of hear.

One hundred grains of this substance being distilled in a retort gradually raised to a red heat, yielded the following products:

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\* Vol. viii. p. 6179.

+ Jour. de Phys. xxx:. 31 .. 2 Beitroge, iii. 109. § Klaproth, Ibid.

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# BITUMENS.

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they ben its with a bias pintin they ideanon tion only	Grains.
38 cubic inches (German) of heavy inflam- mable air	Inolhan
mable air	- 13.75
4 inches (German) of carbonic acid gas	igmochti
A brown thin bituminous oil	. 73.0
Water slightly acidulous	. 1.5
Charcoal	. 6.25
Ashes	. 5.5

100.00

The ashes consisted of lime and silica, with some iron, SDECICS. sulphate of lime, and alumina \*.

Mr Hatchett supposes the elasticity of this substance to be owing to a quantity of air confined between its pores.

4. The retinasphaltum of Mr Hatchett is a substance hitherto found only accompanying Bovey coal, in Devonshire. It was first mentioned by Dr. Milles; but we are indebted to Mr Hatchett for every thing known respecting its chemical properties.

This substance has a pale brown ochre yellow colour. It is very brittle, and breaks with a vitreous fracture. Its specific gravity is 1.135. When held in the hand for some time, it emits a slightly resinous When heated it melts, smokes, burns with a smell. bright flame, and emits a fragrant odour, at last tainted with a bituminous smell. The melted mass, when cold, is black and brittle, and breaks with a glassy fracture.

Water does not act upon it; but it is partially dissol-

\* Klaproth, Beitrage, iii. p. 110;

dia contra Retinasphaltum;

TWOTH .Y

Pit-toal, of

chree kinds.

#### COMPOUND COMBUSTIBLES.

Book II. Division II. ved by alcohol, potash, and nitric acid; the dissolved portion having the properties of a resin; the undissolved, of asphaltum. Mr Hatchett analysed it, and found it composed of \*.

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Pit-coal, of three kinds.

1. Brown coal,

5. Pitcoal, one of the most useful of all the mineral productions, has been divided by mineralogists into various species, according to its external appearances, and the nature of the strata in which it is found; but in a chemical point of view, its most important varieties may be distinguished into three sets: 1. Those that still contain several vegetable principles, strictly so called, and thus give evident marks of their origin. To this head belong most of the varieties of coal arranged by Werner under the head of brown coal. Mr Hatchett has shown, that in some of the substances belonging to this class there is to be found a portion of wegetable extract; in others, as in Bovey coal, a portion of resin; besides the charcoal and bitumen, which constitute the greatest part of its constituents. From another species of brown coal Klaproth obtained, by means of alcohol, a brown red tincture, which left behind it on evaporation a reddish bitter extract partially soluble in water +. 2. Those kinds of coal that contain no traces of unaltered vegetable principles, but

2. Black coal,

\* Hatchett, on the Change of some of the Principles of Vegetables to Bitumen. Phil. Trans. 1804. † Beitrage, iii. 322.

# BITUMENS.

are composed of various proportions of bitumen and charcoal, contaminated like the former with earthy matter. To this head belong the varieties of coal arranged by Werner under the name of black coal, which abound so much in Britain. Kirwan has given us a very ingenious analysis of several specimens, founded upon the property of nitre to deflagrate with charcoal, but not with bitumen. By throwing coal reduced to small pieces into a given weight of melted nitre, he obtained a deflagration, and judged of the proportion of charcoal present by the quantity of nitre decomposed \*. The following is the result of his analyses. 11 1805 5

100 Parts.	Charcoal.	Bitumen.	Earth.	Sp. Grav.
Gannel coal	75.2	21.7	3.1	1.232
Slate coal	47.6	32.5	19.9	1.426
Whitehaven	57.0	41.3	1.7	1.257
Wigan	61.7	36.7	1.6	1:268
Swansey	73.5	23.1	3.4	1.357
Leitrim	71.4	23.4	5.2	1.351
Newcastle	58	40	• 2	1.271

A number of experiments on the constituents of different specimens of British coal have been lately published by Mr Mushet +. He subjected the coals to distillation in close vessels, and thus ascertained the portion of volatile matter which they contained. By burning the coals he determined the portion of earthy matter in each." The following Table exhibits the result of his experiments.

> \* Kirwan's Mineralogy, ii. 514. + Phil Mag. XXXII. 140.

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#### COMPOUND COMBUSTIBLES.

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further state and state out on the second further further to	
Volatile Matter, Charcoal, Ashes, of the of the coal, cole	1
Matter, Matter, Coal. coke.	ET.
and a mark in River Minner and Samo	da
Welsh furnace coal 8.5 88.068 3:432 1:337 1	5.6
Alfreton furnace coal 45'5 52'456 2'044 1'235 water	an
Butterly furnace coal 42.83 52.882 4.288 1.264 1.100	IJĊ
Welsh stone coal 8.0089.700 2.300 1.368 1.393	
Welsh slaty coal 9.10 84:175 6:725 1:409	33
Derbyshire cannel coal 47.00 48.367 4.638 1.278	da
Kilkenny coal 4.25 92.877 2.873 1.602 1.656	8
Stone coal under basalt 16.66 69.740 13.600	12
Kilkenny slaty coal 13.00 80.475 6.525 1.445	
Scotch cannel coal 56.57 39.430 4.000	
Boolavooneen coal 7 13.80 82.960 3.240 1.436 1.596	5
Corgee do Frish 9.10 87.491 3.409 1.403 1.656	5
Queen's county do. ) 10.30 86.560 3.140 1.403 1.621	8
Stonewood, Giant's Caus. 33.37 54.697 11.933 1.150	
Oak wood	-

3. Glance

3. Those kinds of coal which neither contain traces of unaltered vegetable principles nor of bitumen, but seem to consist entirely of charcoal contaminated with some earthy matter. To this head belong the different varieties of coal arranged by Werner under the name of glance-coal. This kind of coal is less common than the preceding. It is remarkable for its metallic lustre, and for the slowness with which it consumes. Many specimens of this coal have been subjected to chemical analysis; the result was always the same. I shall subjoin a few specimens \*.

\* The first analysis by Kirwan (Mineralogy, ii. 528.) The others published by Hericard de Thury. See Gehlen's Jour. v. 323.

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#### BITUMENS.

100 Parts	Charcoal.	Earth.	
Kilkenny coal	97.3	3.7	
Anthracite	90.0	10.0	4
Ditto	72	20	
Ditto	97.25	2.75	
Coal of Notre Dame de Vau	x 78.5	20	

When coal is distilled, the products vary according to the class to which the mineral belongs. The coals of the third class yield no volatile products whatever. Those of the second give out abundance of heavy inflammable air ; a bituminous oil, at first fluid, then of the consistence of tar; and water impregnated with am-The residue is coke, a species of charcoal apmonia. plied with the greatest advantage to many of our manufactures. It burns long and equally, and yields a great deal of heat. The oil has been applied by Lord Dundonald to the various purposes of varnish. Coals belonging to the first class yield abundance of heavy inflammable air, a bituminous oil, and water either very slightly impregnated with ammonia, or containing a quantity of acetic acid, as has been ascertained by the experiments of Klaproth and Hatchett.

Products from coal.

Vol. II.

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> the shortest residue combinations. Theran and the state of a destance of the state of the

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Book II. Division II.

# CHAP. V.

#### REMARKS ON THE PRIMARY COMPOUNDS.

SUCH are the properties of the PRIMARY COMPOUNDS; a class of bodies which has been longer known than any other, which has been examined with peculiar care, and which comprehends many of the most important instruments of chemical investigation.

Division.

The substances included under the name of primary compounds were divided into four sets; namely, oxides, acids, colorific acids, and compound combustibles. The two first sets are counterparts to each other; both are composed of the same ingredients, and both admit of the same subdivisions. They consist of oxygen united to the simple combustibles, incombustibles, or metals, and are distinguished by their acid properties, or the want of that characteristic. They may be divided into products of combustion, supporters of combustion; and combustibles.

Products of combustion.

Every known product of combustion is a primary compound; for it is remarkable, that in all cases of combustion, the bodies which undergo it, however complicated at first, always arrange themselves so as to form the simplest possible combinations. The apparent exceptions consist of substances which have not in reality

#### PRIMARY COMPOUNDS.

tindergone combustion. All the products of combustion known at present are the following :

- 1. Water ;
- 2. Carbonic acid ;
  - 3. Acid of phosphorus ;
  - 4. Acid of sulphur ;
  - 5. Metallic oxides.

In like manner all the *known supporters* of combustion Supporters belong to this class, and are of course primary compounds, excepting oxygen itself. These substances are all decomposed by the action of heat; a property which distinguishes them very readily from the products. The following are all the supporters known to exist, excepting oxygen.

- 1. All the compounds of azote with oxygen:
- 2. All the compounds of muriatic acid with oxygen:
- 3. The metallic acids.

The nature of the combustible oxides and acids has been but imperfectly investigated. Considerable obscurity still hangs over them. As chemical agents, they are inferior in importance to oxide and acid products and supporters, and much more liable to undergo changes in their constitution. With a few exceptions, they are triple compounds, containing exygen united to two combustible bases, most commonly hydrogen and carbon. Sometimes azote seems to enter into their constitution:

The colorific acids; strictly speaking; belong to the same class; and were separated merely on account of the different purposes to which they are applied in chemical investigations.

Colorifie' acide.

The compound combustibles, there is every reason to K k 2 1000

#### PRIMARY COMPOUNDS.

Book II. Division II.

Compound combustibles.

believe, are more variable in their constituents than the preceding classes, and accordingly are more liable to change th ir nature. Chemists have not yet been able to anal se them in a satisfactory manner; but the present state of our knowledge leads us to conclude, that as far as their constituents are concerned, they may be arranged under three classes; namely, 1. Those that are composed of bydrogen and carbon. Ether and the volatile oils, when in a state of purity, seem to belong to this class. 2. Those that are composed of bydrogen, curbon, and oxygen. This appears to be the case with alcohol, with most of the fixed oils, and with those volatile oils that have been exposed to the air, or are beginning to lose their fluidity. These oils, by this change, lose their smell and most of their distinguishing qualities; but they are in some measure restored by distillation with ether, which seems to bring them back to their first condition. 3. Those that are composed of bydrogen, carbon, oxygen, and azote. This appears to be the case with the bitumens; at least if we are to judge from the oil, water, and ammonia, which they yield when distilled.

#### FECONDARY COMPOUNDS.

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Book II. Division III

### DIVISION III.

#### OF

# SECONDARY COMPOUNDS.

By the term Secondary Compound is meant a combination of salifiable bases or primary compounds with each other. These combinations are numerous. Thus acids combine with alkalies, with earths, and with metallic oxides, and form compounds called salts; the earths combine with the fixed alkalies, and form glass; oils combine with alkalies, and form soaps. These combinations come now under our consideration.

The secondary compounds, as far as we are at present acquainted with them, may be arranged under the five following classes.

1. Combinations of earths with each other, and with Arrangemetallic oxides.

ment.

- 2. Combinations of earths with alkalies.
- 3. Combinations of acids with alkalies, earths, and metallic oxides.
- 4. Combinations of sulphureted hydrogen with alkalies, earths, and metallic oxides.
- 5. Combinations of oils with alkalies, earths, and metallic oxides.

#### SECONDARY COMPOUNDS.

Book II. These compounds shall be the subject of the five suc-Division III. ceeding Chapters, under the following titles.

1. Combinations of earths.

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hwe following

- 2. Glass.
- 3. Salts.
- 4. Hydrosulphurets.
- 5. Soaps.

#### COMBINATIONS OF EARTHS.

CHAP. I.

## OF COMBINATIONS OF EARTHS.

SEVERAL of the earths are capable of entering into combination with each other and with metallic oxides, and of forming compounds distinguished by various names according to their external appearance. Some of these combinations are formed into vessels known by the names of *stoneware*, *porcelain*, *enamel*, &c. many of which are of great importance in manufactures and domestic economy.

This class of bodies is of the highest importance; but it has not hitherto been examined by chemists with that degree of attention to which it is entitled. A few only of the compounds into which the earths and the metallic oxides are capable of entering have been formed, and still fewer of these have been described with precision. The subject indeed is difficult, and till lately was not susceptible of accuracy, because the properties of the earths, and the methods of obtaining them pure, were unknown. It is true, indeed, that the greater number of these compounds exist ready formed in the mineral kingdom, constituting the solid basis of this globe of ours. But notwithstanding the rapid progress which the analysis of minerals has lately made, it is -still very uncertain whether it would be safe to trust altogether the result of these analyses; especially as we

Imperfectly known.

Chap. I.

#### SECONDARY COMPOUNDS.

Book II. Division III.

are not able to form artificially compounds similar to those which exist ready formed in the earth.

It will be better, therefore, to refer the consideration of these numerous native compounds to the Second Part of this Work, and to satisfy ourselves at present with a general view of the compounds which the earths are capable of forming, a description of those mixtures which are employed in the manufacture of stoneware and porcelain, and an account of those combinations of earths and metallic oxides which form the different enamels with which these substances are covered. These topics will form the subject of the two following Sections.

## SECT. I.

## OF EARTHY COMBINATIONS IN GENERAL.

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THAT several of the earths have a strong affinity for each other, and are therefore capable of forming combinations, is a fact now well known to the chemical world: Difficulty of But it is by no means an easy matter to form these combinations artificially. If the earths be mixed together in a state of powder, they do not combine intimately; and as few of them are soluble in water, recourse cannot be had, except in a very few cases, to the intervention of that liquid. Chemists, therefore, when they wish to combine the earths together, have scarcely any other agent to employ except fire. This agent answers exceedingly well in combining the metals with each other, and converting them into alloys: But with

combining earths.

#### COMBINATIONS OF EARTHS.

respect to the earths the case is very different; for no fire which can be produced is sufficiently violent to melt a considerable quantity of any of the earths, barytes and strontian excepted.

It is true indeed that silica, and perhaps all the other Their fuearths, may be melted by a process invented by Saussure. He cements a very minute particle of quartz, or any other substance whose fusibility is to be tried, to a slender fibre of cyanite\*, and exposes it in that state to the action of the blow-pipe. He supposes the intensity of the heat inversely proportional to the diameter of the globule produced. Any heat therefore whatever may be communicated by means of the blow-pipe, by diminishing sufficiently the bulk of the particle subjected to its action. The limit of intensity is when the particle cannot be farther diminished without 'rendering the globule produced too small to be seen distinctly by a microscope, and to be measured by means of a micrometer. Saussure found that the heat necessary to melt quartz is equal to 4043° Wedgewood ; that which melts alumina is 18900° Wedgewood †.

The temperature, then, at which the earths melt is Lowered by inconceivably high : but the quantity of these bodies which can be in this manner subjected to experiment, is by far too minute to draw much satisfactory information from it respecting the nature of the compound which the earths are capable of forming with each other. Luckily it is in many cases not necessary to have recourse to it. It is well known that several of the me-

sing temperature.

Chap. I.

mixture.

P. Hatterry

\* This is a blue coloured transparent stone, to be afterwards described. 1 Jour. de Phys. xlv. 3.

Book II. Division III.

tals, which require a very high temperature to bring them to fusion, melt readily when mixed with a portion of some other metal. Thus platinum, the most infusible of them all, melts readily when combined with arsenic. The same thing happens with several of the earths, as Kunkel first discovered : alumina, for instance, though perhaps the most refractory of them all, enters very speedily into fusion when mixed with a proper proportion of silica and lime. Chemists have taken advantage of this property. They have mixed the earths together in various proportions, and then subjected them to heat. The affinity between them was judged of by the degree of fusion which they underwent. Mr Pott was one of the first chemists who laid open this method of proceeding. His Lithogeognosia, which was published in 1746, must have been the result of immense labour. It may be considered as the harbinger of all the mineralogical discoveries which followed. Achard \* of Berlin published, in 1780, a long list of experiments, in which he exposed various mixtures of earth to the heat of a porcelain furnace. This was the first direct set of experiments on the combinations of earths; for Pott, and Macquer and Darcet who followed him, had confined themselves to native combinations. Mr Kirwan, in 1794, published a still more accurate set of experiments + on the same subject. Since that time the combination of the earths has occupied the attention of Morveau 1; not to mention the interesting experiments of Klaproth § and Saussure II.

§ Klaproth's Beitrage, i. 1. || Jour. de Phys. 21v. 3.

History.

<sup>\*</sup> Mem. Berlin, 1780, p. 69. + Miner. slogy, i. 49.

<sup>‡</sup> Jour. de l'Ecole Polytechn. 1. iii. 298. and Ann. de Chim. xxxi. 246.

#### COMBINATIONS OF EARTHS.

and the ingenious speculations of Saussure and Dolomieu \*. But the most important experiments on this subject are those of Darracq + and Chenevix 1; because they have been made with substances in a state of purity, and with the proper precautions to prevent erroneous results. From the experiments of these philosophers, and from the accurate mineralogical analyses of Klaproth and Vauquelin, the following consequences may be drawn.

1. There is an affinity between most of the different Action of earths : But this affinity varies considerably in intensi- on each. ty. Certain earths combine readily with each other in almost every situation, while others cannot be combined without difficulty. There are some combinations of earths which are found native and abundant; others, on the contrary, seldom or never occur.

2. Certain earths when mixed together become very fusible, while other mixtures are as refractory as the simple earths themselves. The affinity between the earths must not be judged of by this increase of fusibility; for several earths which have a strong affinity for each other do not form fusible mixtures at all. In general, mixtures of earths are fusible only when mixed in certain determinate proportions.

3. The three alkaline earths, lime, barytes, and strontian, resemble one another in their disposition to unite with the other earths. Like the alkalies, they combine with alumina and silica, but show no affinity for magnesia nor for each other. Their action on the new earths has not been examined.

+ Ann. de Chim. xl. 52.

Jour. de Phys. xlv. 3. passim. t Phil. Trans. 1802.

the earths other.

Alkaling earths.

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Chap. I.

#### SECONDARY COMPOUNDS.

Book II. Division III. I. Barytes.

When barytes and alumina are boiled together in a sufficient quantity of water, they combine, and form two compounds : one of which, containing an excess of barytes, remains in solution; the other, containing an excess of alumina, is in the state of an insoluble powder. When barytes and silica are fused together in a platinum crucible, they combine, and form a friable blistered mass, of an apple green colour, which is soluble in all the acids, but imperfectly soluble in water. If this compound be boiled in water, it separates into two portions: one, containing an excess of barytes, dissolves, but the presence of the silica prevents the barytes from crystallizing; the other remains in the state of an insoluble powder. Barytes, purified in the usual way, always contains a portion of silica, which it probably takes from the crucible in which it is prepared \*. So great is the affinity of barytes for silica, that it separates silica from potash +. The affinity between alumina and barytes is not strong enough to separate these two earths when the solutions of them in the same acid are mixed together. Muriates of barytes and alumina, for instance, when mixed together, afford no precipitate, provided the salts be pure ‡.

Barytes is usually found native combined with acids; but it occurs sometimes united to silica; and the *staurolite*, which is a transparent crystallized stone, is a compound of silica, alumina, and barytes.

2. Strontian. 4. Strontian resembles barytes exactly in its affinities

to a state i dest detters

\* Vauquelin, Ann. de Chim. xxix. 273. † Morveau, Ibid. xxxi. 248. † Darracq, Ibid. xl. 57.—Chenevix on Corundum, p. 17.—Phil. Trans. 1802.

#### COMBINATIONS OF EARTHS.

for the earths. It unites precisely in the same way Chap. I. with alumina and silica, and precipitates silica from potash. It shows no tendency to unite with magnesia; nor is its affinity for alumina strong enough to occasion a precipitate when the muriates of strontian and alumina are mixed together. It shows no tendency to unite with barytes.

Strontian always occurs native combined with acids; at least it has never yet been found united to earths.

5. Like the other alkaline earths, lime has a strong 3. Lime. affinity for alumina and silica. Scheele first observed, that when alumina is mixed with lime-water, it combines with the lime, and leaves the water in a state of purity \*. The compound thus formed is insoluble in water. Chenevix has shown, that this affinity between lime and alumina facilitates the solution of lime in a fixed alkali. When a solution of potash is boiled upon pure lime, no more of it is dissolved than would have been taken up by the water alone which holds the potash in solution; but when potash is boiled in a mixture of lime and alumina, this last earth is dissolved, together with a much greater proportion of the lime than can be ascribed to the action of the water alone +. The affinity, however, of these two earths for each other is not strong enough to occasion a precipitate when their solutions in the same acid are mixed together. Thus no precipitate falls when muriates of lime and alumina are mixed ‡.

Gadolin first remarked that lime-water forms a pre-

<sup>#</sup> Scheele, i. 196. + Phil. Trans. 1802, p. 346. ‡ Darracq, Ann. de Chim. xl. 58. and Chenevix, Ibid.

#### SECONDARY COMPOUNDS.

Book II. Division III. cipitate with a solution of silica in potash; and Morveau ascertained that this precipitate is a compound of the two earths. This has been confirmed by the experiments of Darracq and Chenevix.

Lime indicates no tendency to combine with the other alkaline earths. It occurs most frequently native combined with acids; but it constitutes likewise, not unfrequently, a constituent part of stones, and in that case it is combined with other earths. If we except the *tremolite*, which is a compound of silica and lime, or perhaps rather carbonate of lime, and which sometimes contains soda, all the earthy compounds containing lime consist of three ingredients, namely, silica, alumina, and lime. The different varieties of zeolites afford examples of this compound.

4. Magnesia.

6. Magnesia has a very marked affinity for alumina; but it shows no tendency to unite with any of the other earths. This affinity was first pointed out by Mr Chenevix in his analysis of magnesian stones\*. When magnesia is held in solution by acids, it is only precipitated partially by ammonia; and if there be an excess of acid present, it is not precipitated at all; because ammonia and magnesia form triple salts with acids, which are soluble : But if a sufficient quantity of alumina be present in the magnesian solution, the whole of the magnesia is thrown down in combination with the alumina. In the same manner, when an alkaline carbonate is poured into a solution of magnesia, no precipitate is formed, because the carbonic acid evolvedis sufficient to hold the whole of it in solution; but if

\* Ann. de Chim. xxviii. 189.

alumina be present, the alkaline carbonate throws down both of the earths in combination. When potash is boiled upon this compound of magnesia and alumina, only a very small proportion of the alumina is dissolved; the greater part being retained by its affinity for the magnesia. By dissolving the residuum in muriatic acid, and precipitating by carbonate of potash, a portion of the magnesia is retained in solution. Potash boiled on the residue dissolves a new dose of alumina. By repeating these processes alternately, the two earths may be separated from each other \*. Thus we see that the action of magnesia on alumina is the reverse of the action of alumina on lime; the last promotes the solution of the lime, whereas the first prevents the solution of the alumina.

Magnesia, when mixed with silica, forms a fusible compound; but the mixture of this earth with barytes, with strontian, with lime, or with alumina, is not fusible in the heats of our furnaces.

Magnesia is frequently found native combined with the other earths. These native combinations consist sometimes of two earths, sometimes of three, and in general some metallic oxide is also present. They may be comprehended under three classes :

1. Alumina and magnesia,

2. Silica and magnesia,

3. Silica, alumina, and magnesia.

To the first of these classes belongs the *ruby*; to the second, *steatites* and *kiffekille*; to the third, the *cyanite* or *sappare* of Saussure. A soapy feel, and a certain

# Chenevix on Corundum, p. 17.

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Chap. I.

Book II. Division III. degree of softness and opacity, has been considered as a characteristic of the earthy combinations which contain magnesia; but the ruby and cyanite are both of them transparent and hard. It is worthy of attention, that magnesia enters into fewer fusible compounds than any of the alkaline earths.

5. Alumina,

7. Alumina, as has been already remarked, has an affinity for all the alkaline earths. It has also an affinity for silica. When silicated and aluminated potash are mixed together, the mixure in about an hour becomes opaque and gelatinous, evidently in consequence of the combination of the two earths \*. When this precipitate is dried and analysed, it yields both silica and alumina. The presence of alumina, as Mr Chenevix has remarked, facilitates the solution of silica in potash. When a mineral containing both silica and alumina is fused in the usual way with a sufficient quantity of potash, and then dissolved in muriatic acid, a number of white flakes frequently remain, which the acid is incapable of dissolving. These white flakes are pure siliceous earth. Their quantity is greatest when . the proportion of the silica over the alumina is greatest. When the proportion of alumina is considerable, the insoluble residue is less, and in some cases it disappears altogether +.

Alumina enters into fusion with none of the other earths except lime, and not even with the fixed alkalies. In this respect it differs exceedingly from silica; which, from the numerous fusible compounds that it is capable of forming, was formerly called the *vitrifiable earth*.

\* Morveau, Ann. de Chim. xxxi. 248. + Ibid. xxviii. 203.

But alumina enters into several triple earthy mixtures which are fusible. Thus mixtures of alumina and silica with any of the alkaline earths, and with magnesia, are fusible.

Alumina is found native in great abundance, and almost always combined with other earths or with metallic oxides, for which it has a very strong affinity. The native earthy combinations, of which it constitutes an ingredient, may be divided into six classes. These are,

1. Alumina and magnesia,

2. Alumina and silica,

3. Alumina, silica, and barytes,

4. Alumina, silica, and lime,

5. Alumina, silica, and magnesia,

6. Alumina, silica, and glucina.

To the first of these classes belongs the *ruby*; to the second, *mica*, *chalcedony*, &c.; to the third, *staurolite*; to the fourth, *zeolites*; to the fifth, *cyanite*; and to the sixth, the *emerald*. These minerals will be described hereafter. All the compounds into which a considerable portion of alumina enters are pretty heavy, and several of them are exceedingly hard.

8. Silica, as we have seen, has an affinity for the alkaline earths and alumina. It has likewise an affinity for zirconia. When a mixture of this last earth and silica is heated strongly, it shows a tendency to fusion \*. It fuses, as we have seen already, with barytes, strontian, lime, and magnesia; so that alumina is the only earth hitherto tried with which it does not enter into fusion.

\* Morveau, Ann. de Chim. xxxi. 259.

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some of which will early miles out counderation of-

6. Silica.

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Chap. J.

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Silica is found native more abundantly than any of the other earths. It also enters into a greater variety of combinations, but almost always with earthy bodies. The combinations of which it is known to constitute a part may be reduced under eight classes ; namely,

- I. Silica and alumina,
- 2. Silica and lime, 3. Silica and magnesia,
  - 4. Silica and zirconia,
  - 5. Silica, alumina, and lime,
  - 6. Silica, alumina, and magnesia,
  - 7. Silica, alumina, and glucina,
  - 8. Silica, alumina, and barytes.

All of these classes have been mentioned already, and instances given of minerals belonging to each, except the fourth, to which belong only the zircon and the byacinth. second, micro, chale alon

The most beautiful earthy combinations are those which consist chiefly of silica and alumina. To that class belong almost all the gems. The combinations of these two earths are also the most useful; for they constitute the basis of porcelain, stoneware, glass pots, and all the different earthen utensils.

Combina. tions of metallic oxides and earths.

9. Several of the earths are capable of combining likewise with metallic oxides, and of forming compounds ; the nature of which has scarcely been examined by chemists. All the oxides which fuse readily into a glass are capable, in that state, of combining with earths by the assistance of heat, and of forming opaque compounds, known by the name of enamels ; some of which will come under our consideration afterwards.

Hitherto only six metals in the state of oxides have Chap. I. been found native combined with earths. These are,

1. Chromium, 4. Zinc,

2. Nickel, 5. Manganese,

3. Copper, 6. Iron.

Chromium constitutes very frequently the colouring 1. Chromis matter of the ruby, in which it is combined with alumina and magnesia; but this metal does not appear to have any remarkable tendency to combine with earths except when it is in the state of an acid.

Nickel has been detected by Klaproth in the chryso- 2. Nickel. prase, and in the green matter called pimelite which sometimes accompanies it; but whether the combination is chemical, or merely a mixture, has not been asmanganese obears marive combined with certained.

The oxide of copper shows no peculiar tendency to 3. Copper. unite with earths, and hitherto it has been detected in one earthy compound only; namely, the smaragdite, a mineral which contains 1.5 per cent. of oxide of copper. But whether this oxide be chemically combined or merely mixed with the other ingredients is not known.

The oxide of zinc has been found native combined, 4. Zinc. with silica in different varieties of calamine. That these bodies are chemically combined has been demonstrated by Mr Smithson in his valuable paper on calamines \* untilstere eleganite qu'abratado ana coberte en

It has been found likewise combined with alumina in a singular mineral lately analysed by Ekeberg, to which he has given the name of automalite. This mineral is of a dark green colour, crystallized in octahedrons

> \* Phil: Trans. 1803. L12

Book I'. Division III. composed of thin plates, which have some transparency, though the entire crystals are opaque. It is harder than quartz; its specific gravity varies from 4.1777 to 4.3714 (but the specimens tried were not pure). Its powder has a light green colour. Before the blow-pipe it does not melt nor change its colour; but with borax it melts into a glass, colourless when cold, but green while hot This mineral, which has some resemblance to the *spinel*, was found composed of 60 parts alumina and  $24\frac{7}{4}$  oxide of zinc;  $9\frac{7}{4}$  oxide of iron, and  $4\frac{3}{4}$  silica \*.

5. Manganese. But it is in the oxides of manganese and iron, especially the latter, that the affinity between the earths and metallic oxides is most conspicuous. The oxide of manganese occurs native combined with barytes; and it is usually a constituent of the black and dark red coloured stones, as *schorl*, garnet, &cc. But when combined with earths, if we except barytes, it forms, in all cases hitherto observed, a very small proportion of the compound.

6. Iron.

The oxide of iron is one of the most common constituents of minerals. It is found in a state of combination with almost every earth. To it indeed, in most cases, is the colour of minerals to be ascribed. No less than seven distinct colours, besides a great variety of shades, are observed in minerals containing iron; and to the iron in most cases is the colour to be ascribed. These colours are,

- 1. White ...... The sommite, &c.'
- 2. Black.....Obsidian

\* Gehlen's Jour. v. 442.

- 3. Green ..... Euclase, thallite
- 4. Blue.....Lazulite, native prussian blue
  - 5. Red......Garnet, ruby
- 6. Yellow......Topaz

From the experiments of Kirwan\*, we learn that iron forms a fusible mass when mixed with barytes, lime, alumina, and silica, when it exceeds the proportion of earth considerably. With magnesia it forms an enamel, but scarcely fuses completely. It renders a mixture of alumina and silica fusible at a very low heat when in the proper proportion. 1. and to old shares

10. During the fusion of several mixtures or combi- Earthy nations of earths, especially those which are found native, the mixture very often frothes considerably, and froth duemits a great number of air bubbles. The emission of these air bubbles can only be referred to one or other of three causes. Either a quantity of water leaves the mixture in the form of steam, or the metallic oxides. which are almost always present, are reduced, and allow their oxygen to escape in the form of gas; or, lastly, the earths themselves undergo some change, and let go a portion of their oxygen in the form of gas. It is probable that the phenomenon is partly owing to all these causes; for these earthy mixtures are much lighter after having been exposed to the action of the fire than they were before. Thus a mixture of equal parts of silica and magnesia, after being heated to 134° Wedgewood, lost 0.135 of its weight; and a mixture of equal parts of alumina and barytes

> + Samanno, Lane, dr. Phys. Riv. 16 \* Mineralogy, i. 58.

-.007

compounds sometimes ring fusion.

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Chap. I.

Book II. Division III. lost in the same situation 0.275 of its weight\*. Now so great a loss as this cannot be ascribed to any other cause than the evaporation of water.

Again, several minerals which are coloured by a metallic oxide become transparent when exposed to a very violent heat; a change which must be occasioned by the revival or dissipation of the metal. This is the case, for instance, with the brown obsidian lava of Dolomieu, with the lazulite, and with schorl †. Now it is exceedingly difficult to free the earth completely from all metallic bodies; especially alumina, the earth most remarkable for giving the property of frothing to earthy mixtures.

Concerning the third cause of the frothing of minerals, namely, the decomposition of the earths themselves, nothing like precision could be expected till the component parts of the earths were discovered. Humboldt announced some time ago, that the earths have the property of absorbing oxygen from the atmosphere. In that case the frothing might, in some instances at least, be ascribed to the emission of this oxygen on the application of heat; but the experiments of Humboldt have been tried without success by Saussure, Fabroni, Champy. Berthollet, and Delametherie t. He has lately, however, announced that he has repeated his experiments successfully in concert with Gay-Lassac; he even declares his belief that earths are capable of combustion as well as other bodies §. Mr Humboldt has not yet published a detailed account of these latter ex-

\* Morveau, Jour de l'Ecole Polytechnique, I. iii. 306.

+ Saussure, Jour. de Phys. xlv. 16. ‡ Ibid. lii, 60,

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§ Gehlen's Jour. v. 232,

periments; of course; we are ignorant of the way in which they were performed, and of the degree of probability which they give to his opinion: an opinion concerning which it would be unfair to decide without farther evidence.

We now know from the discoveries of Mr Davy, that the bases of the alkaline earths are very combustible metals. These earths of course are products of combustion, and therefore incombustible. If Mr Humboldt's opinion referred to the bases of these earthy bodies, it was correct; but if it referred to the earths themselves, it was erroneous. de duido Brig withinst to san

11. There is another phenomenon respecting the fu- Sometimes sion of earthy combinations which has not been hitherto explained. Some minerals, when exposed to the action of heat, melt very readily, and generally with a good deal of frothing; but if the heat be continued, they soon become solid again, and do not fuse unless the temperature be considerably augmented. This is the case with prebnite, thallite, and some felspars. Thus the prehnite undergoes its first fusion at 21° Wedgewood, its second not till it be heated to 81° \*. It cannot be doubted that in this case some one or other of the ingredients which contributed to the first fusion must be driven off; especially as the mineral after fusion loses entirely its original appearance and properties. The late important experiments of Sir James Hall. on the exposure of carbonate of lime to strong heats, under such a pressure as prevents the escape of the carbonic acid, have shown that this substance, under these

\* Saussure, Jour. de Phys, xlv. 14.

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circums'ances, acts the part of a flux, and contributes to the fusion of the carbonate of lime, which he has accomplished in a great variety of instances. It would not be surprising if the first fusion of the zeolites were owing to the presence of carbonic acid, and the frothing to the escape of that substance. This conjecture seems to have struck Sir James Hall, whose skill in that difficult department of chemical investigation will no doubt ehable him in a short time to confirm or refute it.

12. A change no less curious is produced on the appearance and fusibility of some minerals by the slowness or rapidity with which they are cooled after being subjected to fusion. Whinstone (greenstone of Werner), for instance, is a mineral which fuses when raised to a temperature between 40° and 55° Wedgewood. If it be allowed after fusion to cool rapidly, it is converted into a dark-coloured glass much more fusible. than the original whinstone; but if it be made to cool very slowly, it assumes an appearance which has some resemblance to the original whinstone. In this state it is much less fusible than the glass. Sir James Hall, the discoverer of this curious fact, has given the whin in this last state the name of crystallite, a term suggested by Dr Hope. Thus the rock on which Edinburgh Castle is built fuses at the temperature of 45° Wedgewood. By rapid cooling it is converted into a glass which melts at 22°; by slow cooling into a crystallite which melts at 35°. The whin of Salisbury Craig fuses at 55°; its glass at 24°; its crystallite at 38°\*. Lavas agree with these minerals in this respect. The

\* Edin. Trans. V. 75.

Often depends on cooling.

following Table exhibits the degree of Wedgewood's pyrometer at which the rocks tried by Sir James Hall undergo fusion in their natural state, in the state of glass, and in the state of crystallite \*.

Substances.	Original State.	Glass.	Crystal- lite.
Whin of Bell's Mills quarry,	ninaim	dunco	asatin a
(greenstone),	40°	15°	320
Whin of Edinburgh Castle, (por-		and and	1
phyry slate),	45	22	35
Columns, Arthur Seat, (gr. stone),	55	18	35
Whin near Duddingston Loch,	againg	d ethno	timino
(greenstone),	43	24	38
Whin of Salisbury Craigs, (ditto),	55	24	38
Whin from Water of Leith,	Col cost (b)	rome	o (abça) 3
(ditto),	55	16	37
Whin of Staffa, (porphyry slate),	38	141	35
Lava of Catania,	33	18	38
Lava of Santa Venere, Piedi-	A CONTRACTOR	a costa	interes de
monte,	32	18	36
Lava of La Motta,	36	18	36
Lava of Iceland,	35	15	43
Lava of Torre del Greco,	40	18	28
Lava of Vesuvius, 1785,	18	18.	35

Sir James Hall has ascertained, that the crystallization of these bodies depends upon the length of time they are allowed to remain in a higher temperature than that in which the vitreous fusion takes place. A minute or two is sufficient to induce the change; but it is more complete the higher the temperature is above the point of vitreous fusion while the crystals are form-

\* Edin. Trans. v. 75.

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II. ing; provided always it be not so high as to prevent the crystals from shooting.

The striking difference in the fusibility of these bodies seems to depend upon the way in which the component parts of the mineral are combined. When cooled rapidly, these component parts have not time to combine according to their affinities, but are huddled irregularly together. Of course the force of the affinities of those component parts which have a tendency to combine, must conspire with the action of the fire to destroy the cohesion of the parts; the consequence of which must be fusion. Whereas in the crystallite, the component parts having had time to combine according to their affinities, instead of conspiring with the divellent action of the fire, oppose it by coinciding with the force of cohesion. In the first case two forces combine to produce fusion; in the second, only one. Something similar to this may perhaps take place in those minerals which undergo a double fusion, the first in a lower heat than the second \*. ...... attalled to synd

\* Upon this subject the reader may consult a curious paper by the late Mr Gregory Watt, whose premature death must be deeply regretted by the cultivators of chemical science. He fused about seven hundred weight of greenstone in a furnace, allowed it to cool slowly, and then examined the various changes it had undergone. See Phil. Trans. 1804.

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## OF STONEWARE.

property prepared, they are little inferior in durability THE distinguishing character of alumina is to contract in bulk, and to acquire the hardness and solidity of a stony body, if it be made up into a paste with water, dried slowly in the open air, and then exposed to the strong heat of a furnace. It communicates this property to the numerous tribe of clays, which are so common in most countries; a property which has doubtless suggested the applying of clays to form various vessels and other bodies for the purposes of the arts and of domestic economy. Clays consist essentially of alumina and silica mixed in various proportions; and baked clay, of course, must be considered as a compound of these two earths. We shall, in the present Section, take a short view of the manufacture of the various substances formed of baked clay. As there is no single term in our language which comprehends all these bodies, I, have given to the Section the title of stoneware, which includes the greater number of them. These bodies may be divided into four sets; namely, bricks and tiles. pots and crucibles, stoneware and porcelain. A detailed account of the manufacture of these bodies would be improper in this place, and is not intended; such a sketch only is meant as may lead the reader to the principles of the art.

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Properties of clay.

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Clay vessels

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The clay.

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### I. BRICKS AND TILES.

Bricks are oblong masses of baked clay, used as a substitute for stones in building, and tiles are prepared for covering the roofs of houses. The use of them may be dated from the most remote antiquity; and when properly prepared, they are little inferior in durability to stony bodies themselves. Many ancient monuments built of brick still remain entire. Tupos of base diadon

Bricks are prepared from the common blue clay, which occurs in abundance in almost all countries. It onght to be of such a nature as not to be liable to fusion when exposed to a strong heat; at least if the bricks are intended to withstand the action of fire. The presence of a portion of lime renders clay fusible. If the clay contains too little sand, the bricks are liable to crack in cooling; too much, on the other hand, prevents the proper degree of cohesion. Hence the goodness of the bricks depends upon the clay of which they are made, which can only be ascertained by experience. It depends also upon the degree of heat employed in baking them. When not sufficiently burned, they are liable to crumble down in a very short time.

Manufacfare of bricks.

The clay is dug out of the earth, and after being exposed for some time to the air is reduced to powder, and formed into a paste with water. The bricks are then formed in moulds, exposed for some time to dry in the open air, and then burnt in a large furnace constructed on purpose. Tiles are formed in the same way. The clay, however, is finer, and it is usually ground in a mill. Bricks and tiles should be impervious to water : They should be capable of withstanding the action

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of heat, and not be subject to moulder. The clay of which these substances are made always contains iron; hence the red colour which they acquire in burning.

## . In Tak manufacture of vessels of stoneware is of very II. POTS AND CRUCIBLES.

For various manufactures it is necessary to have vessels capable of resisting very violent heats without fusion, even when in contact with bodies that act the part of fluxes. This is the case for instance in glass making, and in the smelting of the ores of the difficultly fusible metals, as iron and copper. The glasshouse pots are formed of the purest kinds of clay that can be procured. By pure clay is meant a clay free from lime, and from any great proportion of iron. Sturbridge clay is commonly used for the purpose in this country. To prevent it from contracting too much in bulk when heated, it is mixed with a proper proportion of old pots reduced to powder. The pots are baked in a mould with great attention, and afterwards allowed to dry as slowly as possible. They are afterwards baked in the requisite degree of heat. and a warmin furnering aller

The crucibles used for chemical purposes are pre- Crucibles. pared of similar materials. Sometimes sand is used instead of old crucibles; sometimes plumbago is substituted. The crucibles are then called black lead crucibles \*. parentso of the blocuit, and then of the wine

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\* For a detailed account of crucibles and clay furnaces, the reader is referred to. Baume's Chemistry, iii. 213. The best account of furnaces for chemical purposes which has hither to appeared in the English language, is given by Dr Lewis at the beginning of his Philosophical Commerce of the Arts. Practical chemists will do well to consult that important treatise.

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which these substances are more the substances are inerce the red colour which

Antiquity.

THE manufacture of vessels of stoneware is of very ancient date. It seems to have originated among the Asiatic nations, and was probably carried on in the East from time immemorial, pretty much as it is practised in India at present. It was well known to the Jews, as we learn from the Old Testament, long before the Babylonish captivity. Stoneware vessels differ from each other in their fineness, according to the purity of the materials of which they are composed; and accordingly are distinguished in this country by a variety of names, such as *flint-ware*, *yellow ware*, *queen's ware*, *Wedgewood-ware*; &c.

Vessels of stoneware consist essentially of two parts. 1. The body of the vessel called the *biscuit*. 2. The glassy covering with which it is coated called the glaze.

The biscuit.

The biscuit is composed of two ingredients; the first is a fine white clay, known by the names of *tobaccopipe clay* and *potters clay*, and the second a fine white sand. In this country the sand is procured by calcining flints to whiteness, and grinding them in a mill. The glaze consists of various ingredients according to circumstances. We shall first take a view of the preparation of the biscuit, and then of the glaze.

Method of preparing it. Staffordshire is the county in which the greatest quantity of stoneware is made in Britain. Hence it is often called *Staffordshire ware*. The clay employed in the manufactures is brought from Dorset and Devonshire, and the flints from the south-eastern counties. The clay is reduced nearly to the consistence of milk

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The glane.

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with water, and the liquid passed through lawn sieves gradually increasing in fineness. By this means all the coarse sand is separated, and only the minutest particles of the clay left suspended in the water. The flint, previously ground to a very fine powder between millstones of chert (hornstone), is mixed with water separately, and brought to the consistence of cream. These two liquids containing the clay and the flint are mixed together in various proportions according to circumstances ; the flint liquor, in some cases, amounting to  $\frac{1}{2}$ th, in others to  $\frac{1}{6}$ th of the whole. The mixed liquid, after being well stirred, is let into troughs, and evaporated to the proper consistence. This mixture is then taken out, and kneaded into a fine dough. This part of the process is tedious, but essential; as it is necessary that the whole should be equally mixed; and of the same consistence. The dough thus prepared, is kept for use in damp vaults; from which it is taken as occasion requires, and given to the workmen, who mould it on the lath to the proper shape. The vessels thus rudely formed are in good weather dried in the open air; but in bad weather, in stoves heated for the purpose. When sufficiently, dry to bear it, they are carried back again to the lath to have their asperities taken off, and the exact shape given. They are then allowed to dry as completely as possible. Afterwards they are put into cylindrical earthen vessels, formed of pounded fire-bricks and clay, called seggars ; and when the shape will admit, each seggar is filled with the vessels to be baked, laid one above another. These seggars are piled one above another in a large circular kiln capable of holding a considerable number. When the seggars are put in, the door of the kiln is built up

Book II. Division III. with bricks, and plastered over with clay. A number of furnaces built round the kiln, the flues of which meet in the middle of it, are then kindled, and thus raise the kiln and its contents to a very high temperature. The fire is kept up for 48 hours, and then allowed to go out. The vessels, when taken out, are now in the state of *biscuit*. They resemble a tobacco pipe in appearance, and like it absorb water with avidity. They could not be employed commodiously, on account of this property, till their surface is covered with a glaze.

'The glaze.

The glaze employed to cover vessels of stoneware may be distinguished into three kinds; namely, galena, or sulphuret of lead, common salt, and enamel.

». Galena,

2. Common salt, Galena is employed only to glaze tiles and the coarsest kinds of stoneware. When laid upon the biscuit, and exposed to the proper temperature, the sulphur is dissipated, and the lead oxidized. This oxide has a strong tendency to vitrefy, and in that state to unite with earthy bodies. The brown glaze on the coarse stoneware, then, is nothing else than glass of lead. Such vessels are dangerous when used to contain articles of food, as the glaze is easily corroded and dissolved by acids and various saline bodies.

Common salt is employed to glaze the surface of finer stoneware vessels. The process is curious. When the biscuit is sufficiently baked, a quantity of common salt is introduced into the kiln. The heat converts this salt into a vapour; it penetrates the seggars through holes left on purpose, and surrounds the biscuit with an atmosphere of salt. The salt, by combining with the surface of the biscuit, disposes it to vitrification.

3. Enamel.

Enamel is nothing else than an opaque glass melted over the surface of the biscuit. It consists essentially

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of various proportions of oxide of lead mixed with Chap. I: sand and glass. Mr Wedgewood published the following as the enamel which he used : One hundred parts of lead are melted with from 15 to 40 parts of tin, and the mixture oxidized completely, by exposing it to heat in an open vessel. One hundred parts of this oxide are mixed with 100 parts of a fine white sand, composed of three parts silica and one part of tale, and with about 25 parts of common salt. This mixture is melted, then reduced to powder, and formed into a liquid of the consistence of cream. According to Dr Watson, the yellow glaze used in Staffordshire is composed of 112 parts of white lead, 24 of ground flint, and six of flint glass, mixed with water to the consistence of cream \*. The biscuit is dipt into this liquid and drawn out again; by this means its surface is covered with the solid matter of the enamel, the water being speedily absorbed. The vessels are put into the seggars as before, but a little cross of stoneware is interposed to keep them sepaparate. They are put again into the kiln and heated as at first. The enamel melts into a glass, and spreads equally on their surface. The excellency of a good enamel is, that it easily fuses into a kind of paste at the heat which is necessary for baking stoneware, and spreads equably on the vessel, forming a smooth glassy surface, without losing its opacity, or flowing completely into a glass. Its whiteness depends upon the proportion of the tin, its fusibility upon the lead +.

\* Chemical Essays, ii. 269.

+ For an account of the manufacture of stoneware, the reader may consult Baume's Chemistry, iii. 227, and Watson's Chemical Essays, ils 256.

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## IV. PORCELAIN.

History.

THE finest kind of stoneware, called porcelain, does not differ essentially from the common stoneware just described; but it is more beautiful and more capable of resisting the action of chemical agents, on account of the purity of the substances of which it is composed, and the nature of the enamel with which it is covered. It was early brought to a state of considerable perfection in China and Japan, but the discovery of the art of making it in Europe is of a much later date. Specimens of it were brought first from China and Japan to modern Europe \*. These were admired for their beauty, were eagerly sought after, and soon became the ornaments of the tables of the rich. Various attempts were made to imitate them in different countries of Europe, but the greater number were without success. Accident led to the discovery in Germany about the beginning of the 18th century. A chemist in Saxony,

\* Porcelain vessels were known to the Romans, and called by them vasa murrhina. They were first brought to Rome by Pompey after the defeat of Mithridates, as we are informed by Pliny (lib. xxxvii. 2.). The Romans were ignorant of the mode of manufacturing them, but imported them from Pontus and Parthia. After the taking of Alexandria, a vessel of porcelain was the only part of the spoil retained by Augustus. That the vasa murrhina of the Romans were the same as our porcelain vessels, has been ascertained, as Whitaker informs us, by the porcelain found in the ruins of the ancient Lyons. The name porcelain, if we believe Whitaker, comes from the French name of the plant portulace oleracea or furstain, which has a purple-coloured flower. It got that name because the porcelain of the ancients was always of a purple colour. See Whitaker's Course of Hannibal over the Alph, j. 55.

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during a set of experiments in order to ascertain the best mixtures for making crucibles, stumbled upon a compound which yielded a porcelain similar to the Eastern. In consequence of this discovery, Saxony soon produced porcelain scarcely inferior to that of Japan in beauty, and superior to it in solidity and strength: But its composition was kept secret; nor were there any accurate ideas respecting the component parts of porcelain among men of science, till Reaumur published his dissertations on the subject in 1727 and 1729.

That celebrated philosopher examined the porcelain of Japan and the different imitations of it which had been produced in France and other parts of Europe. The texture of the first was compact and solid, but that of the imitations was porous. When both were exposed to a strong heat, the first remained unaltered, but the others melted into glass. From these experiments he drew the following ingenious conclusions.

Porcelain owes its semitransparency to a kind of semivitrification which it has undergone. Now it may receive this two ways: 1. Its component parts may be such as easily vitrify when sufficiently heated; but the degree of heat given may be just sufficient to occasion a commencement of vitrification. This porcelain when strongly heated will easily melt. Such, therefore, was the composition of the European imitations of porcelain. 2. It may be composed of two ingredients; one of which vitrifies, but the other is not altered by heat. When a porcelain composed of such materials is baked in a sufficient heat, the fusible partmelts, envelopes the infusible, and forms a semitransparent substance, which is not farther altered by the same degree of heat. Such therefore must be the porcelain

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Chap. I.

Book II. Division III. of Japan. Father Entrecolles, a missionary to China, had sent an account of the Chinese mode of making porcelain, which coincided exactly with this ingenious thought of Reaumur. The ingredients, according to him, are a hard stone called *petunse*, which they grind to powder, and a white earth called *kaolin*, which is intimately mixed with it. Reaumur found the petunse fusible, and the kaolin infusible, when exposed separately to a violent heat.

These notions were not prosecuted farther by Reaumur; but in 1758, the Count de Lauragais, assisted by Darcet and Le Gay, began a set of experiments which were continued for four years, and which led to the discovery of a porcelain possessed of the same qualities with that of China, and inferior only in whiteness. Macquer, who at that time superintended the manufactory of Sevres, advised the French government to propose a reward for the discovery of earthy substances capable of forming a white porcelain. This was done; and in consequnce of it, Villaris, an apothecary of Bourdeaux, announced the existence of a white earth near Saint-Yriex-la-Perche, in the department of the Haut-Vienne, which in his opinion would answer the purpose. It was tried by Macquer with the expected success. A porcelain manufactory was established at Sevres, and at present there are no fewer than 30 in France\*. Different manufactures of porcelain have been successfully established likewise in England; first at Chelsea in the neighbourhood of London, and afterwards in Coalbrook, dale, and in Derby.

· Fourmy's Memoire sur les Ouvrages de Terres cuites, p. 78-

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The essential ingredient of porcelain is a very pure clay known by the name of *porcelain clay*. This is equivalent to the kaolin of the Chinese. Macquer and Baumé, in the course of their experiments, ascertained that very fine porcelain may be made by using the earth of alum instead of clay; but the great expence prevents the possibility of introducing it into the manufacture of that article with advantage. Sometimes porcelain clay consists of materials mixed in such proportions that no addition is necessary; the biscuit made from it being susceptible of undergoing that semivitrification which gives the transparency and compact nature which distinguish porcelain. Such is the porcelain clay of Limoges. According to the analysis of Hassenfratz, it is composed of 62 silica

> 19 alumina 12 magnesia 7 barytes

#### 100\*

> 20 silica 12 moisture 8 loss

> > 100 +

\* Ann. de Chim. xiv. 144.

+ Kirwan's Min.i. 179.

Chap. I. Porcelain carth.

Book II. Division III. Giobert has announced that porcelain earth is sometimes nearly pure magnesia and silica ‡.

When an addition is necessary, the substance used is *felspar*, which is equivalent to the petunse of the Chinese. According to an anonymous German writer, the finest Saxon porcelain is formed by mixing together equal weights of ground felspar and porcelain clay §. The method of forming the biscuit of porcelain is the same as of stoneware, and therefore requires no particular description.

Glaze of Porcelain. Porcelain is always covered with a glaze, composed of earthy ingredients without any mixture of metallic oxides. Hence the high temperature necessary to fuse it, and the property which porcelain vessels have of resisting the action of the most corrosive substances precisely as common glass does. The substance commonly employed is *felspar*; which is composed essentially of silica and alumina united to some potash, to which the fusibility is to be ascribed. This is the glaze said to be used in Sax ny, and, as Brogniart informs us, likewise at the manufactory of Sevres, near Paris.

Method of colouring toneware, Vessels both of stoneware and porcelain are commonly painted of various colours. These paintings are often excellent, both in elegance of workmanship and in brilliancy of colours. The colours are given by means of metallic oxides, which are mixed up with other ingredients proper to constitute an enamel, and applied in the usual manner with a pencil,

‡ Nicholson's Jour. xii. 277.

§ Secret de Prices Forcelains, &c. p. 608, at the end of the French translation of Neri's Art of Gluss-making.

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On this subject much light has been thrown by the experiments of Wedgewood; and Brogniart has lately published a general account of the processes at Sevres, of which he is director \*.

The process differs a little according to the substance on which the colours are to be applied. When the vessels are covered with enamel, less flux is necessary, because the enamel melts at a low heat, and the colours readily incorporate with it. But this renders them more dilute, and makes it often necessary to retouch them. The colours on enamel generally appear brilliant and soft, and are not liable to scale. The flux is either a glass of flint and lead, or borax mixed with flint glass. The colours are usually made into a paste by means of gum water or volatile oils. Some of them are liable to alteration by the action of the lead on them.

The colours applied upon hard porcelain, or porce- Painting on lain glazed with felspar, are nearly the same as those applied on enamel, but more flux is necessary. They are not liable to dilution, as the felspar glaze does not melt at the heat requisite for fusing the colours and their flux. They are liable to scale off when repeatedly heated.

Colours are sometimes applied over the whole surface of the porcelain; the flux in that case is felspar. But such colours are not numerous, because few oxides can stand the heat necessary for melting felspar without being altered or volatilized.

\* Phil. Mag. xiii. 342.

t name

porcelain.

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Book II. Division III. 1. Purple is given by means of the purple oxide of gold precipitated by the smallest possible quantity of muriate of tin. This oxide is mixed with a proper quantity of powdered glass, borax, and oxide of antimony, and applied with a pencil. It cannot bear a strong heat without losing its colour.

2. Red is given by oxide of iron, A mixture of two parts of sulphate of iron and one part of alum is calcined slowly, till it acquires a fine red colour when cold. This powder is mixed with the usual flux, and applied with a pencil.

3. Yellow is given by the oxide of silver, or by oxides of lead, antimony, and sand; green, by the oxide of copper; blue, by the oxide of cobalt; and violet, by the oxide of manganese,

For farther information on this subject, the reader is referred to the dissertation of Brogniart.

Gilding upon porcelain is performed in the same way as painting. The gold is reduced to the state of an impalpable powder by solution and precipitation. It is mixed up to the proper consistence with oil and a small quantity of flux, and applied with a pencil; the vessels are baked a second time. By this the gold is made to attach itself firmly to the vessel, and by the burnisher it acquires the requisite lustre. Klaproth has lately shown, that platinum may be applied upon porcelain with a similar effect. The fine powder of platinum obtained by precipitating the metal by means of sal ammoniac, and exposing the precipitate to a red heat, is to be ground with a little flux and oil to the proper consistence, and applied with a pencil upon the vessels. By

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baking these vessels and burnishing, the platinum ac- Chap. I. quires the requisite lustre \*.

Painting common stoneware vessels would enhance their price too much; but this is avoided by an ingenious mode of copperplate-printing, said to have been first invented by some person in the neighbourhood of Liverpool. The figure which is to be painted on the vessel is engraven on a copperplate in the usual way, excepting only that it is not reversed as is done in common copperplate-engraving. The paint to be applied to the stoneware is brought to the requisite consistence, put upon the copperplate, and the impression 'taken off, as usual, upon moist paper, by means of the rolling press. The paper, while still moist, is applied to the stoneware biscuit and pressed upon it. By dipping the biscuit in water and agitating gently, the paper is washed off without injuring the impression upon the vessel, the paint having been made up with oil. The impression upon the paper was reversed, but upon the stoneware it is precisely as it was cut upon the copperplate. The vessel being now baked, the paint is glazed on, and assumes its characteristic colour and brilliancy. By this contrivance any number of vessels may be easily printed with the same figures in a very short time. This ingenious process seems to be at present confined to Britain; at least none of the foreign stoneware that I have had an opportunity of examining, exhibited any marks of having been printed. Neither has any mention of the process been inserted into any work which I have met with.

\* Nicholson's Jour, vii, 286.

Copperplate-print-

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Specific gravity of stoneware.

The specific gravity of the different kinds of stoneware differs considerably according to the compactness of the texture. The following are the results obtained by Dr Watson \* and Brisson :

	op. grav.
East Indian China +	2.385
East Indian China t	2.346
Limoges porcelain +	2.341
Bristol stoneware ‡	2.340
Flint ware ‡	2.188
Sevres porcelain +	2.146
Yellow ware ‡	1.988
	S. S. Ashan I. M. S.

\* Chemisal Eesitys, ii. 282.

+ Brisson. ‡ Watson.

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### CHAP. II.

#### GLASS. OF

SILICA, when mixed with the fixed alkalies, and exposed to a strong heat, enters readily into fusion. It melts also when heated along with some of the alkaline earths, especially lime, provided a little alumina be present. These mixtures are very ductile while in fusion, and may be readily moulded into any shape we please. If they be suddenly cooled below the temperature at which they become solid, they retain their transparency. and assume those peculiar properties which belong to the substance called glass. Glass then is a combination of the fixed alkalies or alkaline earths with silica, either alone or conjoined with alumina, brought into complete fusion, and then suddenly congealed. Metallic oxides are sometimes added : they assist the fusion like the alkalies, and communicate frequently a peculiar colour to the vitreous mass.

The method of making glass was known at a very History. early period. According to Pliny, the discovery was owing to an accident. Some merchants, with a shipload of soda from Egypt, had cast anchor at the mouth of the river Belus in Phœnicia, and were dressing their dinner on the sand. They made use of large lumps of

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soda to support their kettles, and lighted fires under them. The heat melted the soda and the siliceous sand together, and the result was glass. For some time after this accidental discovery the manufacture of glass was confined to the river Belus. This manufacture seems to have been carried to a considerable degree of perfection among the ancients. They mention drinking glasses, glass prisms, and coloured glasses of various But perfectly transparent glass was considered kinds. as very valuable; for Nero gave L.50,000 for two glass cups with handles; a proof that their processes must have been far less perfect than ours. It was usual for them to melt the materials of their glass into a black mass called ammonitrum, of which statues were sometimes made. This ammonitrum was again melted and purified by refiners. Glass panes seem to have been first used in windows in the third century, but they did not come into common use till long after \*.

Nature of glass.

While glass is in fusion, the substances which enter into its composition may be considered as combined with each other so as to form a homogeneous mass similar to water, holding a variety of salts in solution. If it be cooled down very slowly, the different undency of the constituents to assume solid forms at peculiar temperatures will cause them to separate successively in crystals; just as the salts held in solution in water assume the form of crystals as the liquid is slowly evaporated. But if the glass be quickly cooled down to the point of congelation, the constituents have not

\* See Dr Falconer's paper on this subject, Manchester Memoirs, ii. 95. and Dr Merrets's Preface to his Latin Translation of Neri's Art of Glass-making.

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time to separate in succession, and the glass remains the same homogeneous compound as while in a state of fusion ; just as would happen to a saline solution if suddenly exposed to a cold sufficient to congeal it completely. Hence it appears that the vitreous quality depends entirely upon the fusibility of the mixture, and the suddenness with which it is cooled down to the point of congelation. The substance, though solid, is precisely the same as to its chemical composition as if it were still in fusion; the sudden cooling having fixed the constituents before they had time to assume a new arrangement.

All fusible mixtures of the earths proper with fixed alkalies, alkaline earths, or metallic oxides, may be made at pleasure to assume the form of glass, or the appearance which characterises stone or porcelain, according to the rate of cooling; and glass may be deprived of its vitreous form merely by fusing it, and cooling it down with sufficient slowness to enable the constituents to separate in succession.

Many curious experiments on this subject were Changes in made by Reaumur and Lewis, who pointed out the ing after fumethod of converting different kinds of glass into an opaque, white, hard, refractory substance like porcelain, which is commonly distinguished by the name of Reaumur's porcelain. Dr Lewis, by a variety of experiments, demonstrated that all kinds of glass could not be converted into porcelain. He succeeded only with those that were composed of a variety of constituents \*. The reason is obvious; such glasses alone contain ingredients

it by coolsion.

Chap. H.

\* Phil. Com. of the Arts, p. 230.

Book II. Division III. that become solid in succession. Green glass succeeded best with him. Indeed this glass is very apt to acquire a crystallized form. The temperature best suited to the change is that in which the glass is softened without being melted.

It was the curious experiments of Sir James Hall on basalt and greenstone, detailed in the preceding Chapter, that first explained upon what the vitreous state of substances depends. He found that glass (consisting of various earthy bodies) always loses its vitreous state, and assumes that of a stone, if more than a minute or two elapses while it is cooling down from complete fusion to the point at which it congeals.

Rlate glass.

There are different kinds of glass in common use in this country for various purposes. The finest are plateglass, of which looking-glasses are made, and *flint-glass*, or *crystal*, used for the finest vessels. These are perfectly transparent and colourless, heavy and brilliant. They are composed of fixed alkali, pure siliceous sand, calcined flints, and litharge. The manufacturers conceal the proportions of their ingredients with great care \*.

\* For the fullest account of glass-making, the reader is referred to a treatise on the subject published by Neri, an Italian Dr Merret, an Englishman, translated it into Latin towards the end of the 17th century, and enriched it with many notes. Kunkel translated this Latin edition with Merret's notes into German, and added to the work his own numerous experiments on glass-making, and the verification of all the formulas of Neri. Kunkel's work was translated into French, and published in a quarto volume in 1752. A very elaborate account of glass-making has been published also in the Arts et Metiers, drawn up under the direction of the French Academy. More lately, a small volume on glass-making has been written in Fr neh by Loysell. The processes, as he describes them, differ in many respects from those followed in this country.

The plate glass is poured melted upon a table covered Chap. II. with a sheet of copper. The plate, as cast, is about an inch thick; but it is ground down to the proper degree of thinness, and then polished. The only manufactory in Britain is at St Helens, about 10 miles from Liverpool. Flint-glass contains much oxide of lead. Dr Lewis extracted from it one-fourth of its weight of that metal in a malleable state \*. Though it be very solid, it does not seem to be absolutely impervious to gaseous bodies, at least when heated nearly to the melting point. Dr Lewis surrounded a piece of it with charcoal powder, and kept it for some time in a heat not sufficient to melt it. The lead was revived in drops through the whole substance of the glass +. Dr Priestley ascertained, that glass tubes filled with hydrogen gas, and heated, became black, from the revival of the lead. When alkaline hydrosulphurets are kept in glass phials, the inside is soon coated with a black crust. I am informed by Dr Henry of Manchester, that this black crust is nothing else than lead separated by the sulphur from the glass.

Crown-glass is made without lead. It is therefore Crown much lighter than flint-glass. It consists of fixed alkali fused with siliceous sand. As the earthy matters employed by the glass-makers are seldom quite pure from some mixture of iron or similar ingredient, the glass would have a green colour unless some means were taken to remedy it. The addition of some black oxide of manganese remedies this defect ; hence it is used for that purpose by the glass-makers, and was formerly

\* Neumann's Chem. p. 55. † Neumann, Hid.

glass.

Book II. Division III. called soap of glass. If too much be used, the glass acquires a purple cast; a colour very common in the window-glass made in England. In Scotland the window-glass has always a considerable shade of green.

As no exact analysis has yet been made of the finer kinds of glass, we are not acquainted with the proportion of its constituents. They no doubt vary considerably. As the fixed alkalies are volatilized by a strong heat, it would be worth while to examine whether a portion of them is not driven off while the glass is in fusion, or whether the previous steps of the process prevent that from happening.

Bottle-glass.

Bottle-glass is the coarsest and cheapest kind; little or no fixed alkali enters into its composition. It consists of an alkaline earth, usually lime, combined with alumina and silica. In this country it is composed of sand and the refuse of the soap boiler, which consists of the lime employed in rendering his alkali caustic, and of the earthy matters with which that alkali was contaminated. The following are the ingredients used in the bottle-glass manufactory of Lafond in France:

> > 100 100

A specimen of this glass analysed by Vauquelin was composed of

Silica	
Lime	
Alumina.	
Oxides of	manganese and iron 4
Loss	4
	100

Besides a portion of potash so small that it could not Chap III. be appreciated \*.

Of the different species of glass, the most fusible is flint-glass, and the least fusible bottle-glass. According to the experiments of Saussure, flint-glass melts at the temperature of 19° Wedgewood, crown glass at 30°, and bottle-glass at 47°+. The specific gravity of glass differs considerably according to its constituents. The following are the results obtained by Brisson, as published in the Appendix to Lavoisier's Cheinistry :

> Bottle-glass ..... 2.7325 Green glass ..... 2.6423 White glass ..... 2.8922 St Gobin crystal .. 2.4882 Leith crystal .... 3.1890 Flint-glass ..... 3.3293

The properties that distinguish good glass are well its property known. It is perfectly transparent; its hardness is very considerable; its specific gravity varies from 2.3 to 4, according to the proportion of metallic oxide When cold it is brittle : but at a which it contains. red heat it is one of the most ductile bodies known, and may be drawn out into threads so fine as to be scarcely visible to the naked eye. It is almost perfectly elastic, and of course is one of the most sonorous of bodies. There are but few chemical agents which have any action on it. Fluoric acid dissolves it with great rapidity, and so do the fixed alkalies when as-

\* Jour. de Pbys. 1x. 419. + 1bid. xlv. 14. Nn Vol. II.

ties.

Specificgrad

vity of glassa

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sisted by heat. Dr Priestley has shown also, that the long continued action of hot water is capable of decomposing it: A discovery which explains sufficiently the siliceous earth obtained by Boyle and Margraff when they subjected water to tedious distillations in glass vessels.

Method of making glass.

After mixing the materials of glass together, it is usual to expose them for some time to a moderate heat. This serves several purposes. It drives off all combustible bodies which may happen to be mixed with the sand; it produces a commencement of combination which makes the glass afterwards less liable to corrode the clay pots in which it is melted; and the alkali, by this incipient combination, is not so apt to be volatilized; which might be the case if the materials were exposed at once to a violent heat. The mixture, after being thus heated, is called the frit. Through the domes in which the frit is heated, it is usual to see very thin bubbles of glass passing; a proof that some of the materials are volatilized during this first part of the process.

The frit, while still hot, is introduced into large pots made of a mixture of pure clay and baked clay, and exposed to a heat sufficient to melt it completely. The fusion must be continued till the effervescence occasioned by the separation of the carbonic acid from the soda has subsided; and the opaque scum, known by the name of glass-gall, which collects on the surface of the glass, must be removed. This scum is occasioned by the common salt and other foreign bodies which are always mixed with the soda of commerce. When the fusion has been continued the proper time, the furnace

is allowed to cool a little. In that state the glass is exceedingly ductile, and readily assumes any shape that the workman pleases.

If the glass vessels, after being formed, were cooled rapidly, they would contract unequally, and become in consequence so brittle as to fall to pieces whenever they were handled. To prevent this inconvenience, they are put into a large red hot furnace, which is allowed to cool very slowly to the temperature of the air. This process is called annealing.

Glass is often tinged of various colours by mixing with it while in fusion some one or other of the metallic oxides.

Blue glass is formed by means of oxide of cobalt. Green, by the oxide of iron or of copper.

Violet, by oxide of manganese.

Red, by a mixture of the oxides of copper and iron. Purple, by the purple oxide of gold.

White, by the oxide of arsenic and of zinc.

Yellow, by the oxide of silver and by combustible bodies.

Opticians, who employ glass for optical instruments, Its defects. often complain of the many defects under which it la-The chief of these are the following : bours.

1. Streaks. These are waved lines, often visible in glass, which interrupt distinct vision. They are probably owing sometimes to want of complete fusion, which prevents the different materials from combining sufficiently; but in some cases also they may be produced by the workmen lifting up, at two different times, the glass which is to go to the formation of one vessel or instrument.

Coloured glass.

Chap. II.

### SECONDARY COMPOUNDS.

Book II. Division III. 2. Tears. These are white specks or knots, occasioned by the vitrified clay of the furnaces, or by the presence of some foreign salt.

3. Bubbles. These are air-bubbles which have not been allowed to escape. They indicate want of complete fusion, either from too little alkali, or the application of too little heat.

4. Cords. These are asperities on the surface of the glass, in consequence of too little heat.

SALTS.

CHAP. III.

## OF SALTS.

THE word SALT was originally confined to muriate of Definition. soda or common salt; a substance which has been known and in common use from the remotest ages. It was afterwards generalized by chemists, and employed by them in a very extensive and not very definite sense. Every body which is sapid, easily melted, soluble in water, and not combustible, has been called a salt.

Salts were considered by the older chemists as a class of bodies intermediate between earths and water. Many disputes arose about what bodies ought to be comprehended under this class, and what ought to be excluded Acids and alkalies were allowed by all to be from it. salts; but the difficulty was to determine concerning earths and metals; for several of the earths possess all the properties which have been ascribed to salts, and the metals are capable of entering into combinations which possess saline properties.

In process of time, however, the term salt was restricted to three classes of bodies; namely, acids, alkalies, and the compounds which acids form with alkalies. earths, and metallic oxides. The first two of these classes were called simple salts; the salts belonging to the third class were called compound or neutral. This

Chap. III.

Book II. Division III. last appellation originated from an opinion long entertained by chemists, that acids and alkalies, of which they are composed, were of a contrary nature, and that they counteracted one another; so that the resulting compounds possessed neither the properties of acids nor of alkalies, but properties intermediate between the two.

Ghemists have lately restricted the term salt still more, by tacitly excluding acids and alkalies from the class of salts altogether. At present, then, it denotes only the compounds formed by the combination of acids with alkalies, earths, and metallic oxides\*.

No part of chemistry has been cultivated with more zeal than the salts, especially for these last 40 years. During that time the number of saline bodies has been enormously increased, and the properties of a very great number have been determined with precision. Still, however, this wide and important region is far from being completely explored,

Number of salts. Chemists have agreed to denominate the salts from the acids which they contain: The earth, alkali, and metallic oxide, combined with that acid, is called the *base* of the salt. Thus common salt being a compound of muriatic acid and soda, is called a *muriate*, and soda is called the base of common salt. Now since there are 34 acids and 65 bases, it would appear, at first sight, that there are 2210 salts; but of the 53 metallic oxides at present known there are a considerable number which cannot combine with all the acids. This is

\* The terms salt and neutral salt are often confounded. In this Work the epithet neutral is confined to salts having no excess of acid or base.

the case also with silica, and perhaps with some of the Chap. III. other earths. We must therefore subtract all these deficiencies from the full number 2210. However, to compensate this, at least in part, there are several acids capable of combining with two bases at once. Thus the tartaric acid combines at once with potash and soda. Such combinations are called triple salts, and they in- Triple salts. crease the number of salts considerably. There are some salts, too, which are capable of combining with an additional dose of their acid, and others which combine with an additional dose of their base. The French chemists denote the first of these combinations by adding to the usual name of the salt the phrase with excess of acid, or by prefixing to it the word acidulous : They denote the second by subjoining the phrase with excess of base. This method has the merit of being precise; bur it is awkward and tedious. The ingenious mode of naming these combinations proposed by Dr Pearson ought certainly to be preferred. It is equally precise, if not more so, and far more convenient in every respect. It consists in prefixing to the usual name of the salt the Supersalts preposition super, to denote an excess of acid, and the salts. preposition sub, to denote an excess of base \*. Thus sulphate of potash denotes the salt in its state of perfect neutralization, without any excess either of the sulphuric acid or of the potash; supersulphate of potash is the same salt with an excess of acid; subsulphate of potash is the same salt with excess of base. These three different kinds of salts must increase the number of saline compounds very considerably ; but the precise number

\* Pearson's Translation of the Chemical Nomenclature, p. 52.

and sub-

Book II. Division III. of salts is not known, as many of them remain still unexamined by chemists. Propably there are not much fewer than 2000. Some idea may be formed of the progress which this branch of chemistry has made, by recollecting that 40 years ago not more than 30 salts in all were known.

Of these 2000, however, a considerable number may be considered as still unknown, as they have been merely formed without being examined. Of those which are known, the greater number have not been applied to any use, and therefore do not deserve a very particular description.

Nomenclature. As the different genera of salts are denominated from their acids, it is evident that there must be as many genera as there are acids. The terminations of the names of these genera differ according to the nature of the acid which constitutes them. When that acid contains a maximum of oxygen, the termination of the genus is *ate*; when it does not contain a maximum of oxygen, the termination of the genus is *ite*. Thus the salts which contain sulphuric acid are called *sulphates*; those which contain sulphurous acid are called *sulphates*. This distinction is of some consequence, because the salts differ very much, according as the acid is saturated with oxygen or not. The *ites* are seldom permanent; when exposed to the air, they usually attract oxygen, and are converted into *ates*.

Every particular species of salt is distinguished by subjoining to the generic term the name of its base, Thus the salt composed of sulphuric acid and soda is called *sulphate of soda*. Triple salts are distinguished by subjoining the names of both the bases connected by hyphens. Thus the compound of tartaric acid, pgtash,

and soda, is called tartrate of potash-and-soda. An- Chap. III. other mode of naming these triple salts is sometimes followed. One of the names of the bases is prefixed to the generic name so as to act the part of an adjective. For example, soda muriate of rhodium, means the triple salt composed of muriatic acid, soda, and oxide of rhodium. Sometimes the name of the base prefixed is altered a little, as ammonio-sulphate of magnesia (sulphate of magnesia- and-ammonia); ferruginous sulphate of zinc (sulphate of zinc-and-iron). This is a less unwieldy mode of naming the triple salts, but it is not always possible to employ it in our language.

Before the correction of the chemical nomenclature Arrange, by Morveau in 1781, chemists usually referred the genera of salts to the bases, and distinguished the species by the acids. That celebrated philosopher entirely reversed the method by introducing the new generic terms formed from the acids; and his ingenious nomenclature having been sanctioned and improved in 1787 by Lavoisier, Berthollet, and Fourcroy, who joined with him in forming a new chemical nomenclature. has now become universally prevalent. As far as relates to the salts which have alkaline and earthy bases. this method introduced by Morveau is certainly proper; for in them the acids in a great measure stamp the character of the salt, and therefore ought to constitute the generic distinction. But it does not apply equally well to the salts whose bases are metallic oxides; for in them it is not the acid but the base which stamps the character. In them, therefore, the genera ought to be reversed: they ought to be derived not from the acids but from the bases; or rather from the metals whose oxides constitute the base.

ment.

### SECONDARY COMPOUNDS.

Pook II. Division III. Division into two classcs. The salts, then, naturally divide themselves into two grand classes; the first of which comprehends the alkaline and earthy salts, which derive their most important characters from their acids; the second comprehends the metalline salts, whose bases, on the contrary, stamp their most important properties. I shall therefore divide this Chapter into two Sections: in the first of which I shall describe the alkaline and earthy salts; in the second, the metalline.

SECT. I.

### OF ALKALINE AND EARTHY SALTS.

As the salts belonging to this Section may be arranged with great propriety according to their acids, they naturally divide themselves into 34 genera, every particular acid constituting a genus. But of these genera some must be omitted altogether; because the salts which belong to them have not been examined. Every genus will comprehend under it as many species as there are bases; besides the triple salts and the *subs* and the *supers*.

As these genera are very numerous, it will be attended with considerable advantage to the learner if we subdivide them into sets according to their properties. This is attempted in the following TABLE.

# TABLE of the Alkaline and Earthy Salts.

I. Incombustible Salts.

a. Not altered when heated with combustibles.

- 1. Muriates.
- 2. Fluates.
- 3. Borates.
- .4. Phosphates \*.

b. Decomposed without combustion when heated with combustibles.

- 1. Sulphates.
- 2. Carbonates.

c. Set fire to combustibles, or yield oxygen gas by heat.

1. Nitrates.

2. Nitrites.

3. Hyperoxymuriates +.

4. Arseniates.

5. Molybdates.

6. Tungstates.

7. Chromates.

8. Columbates ‡.

II. Combustible Salts.

a. Acids partially dissipated, leaving salts in ate.

1. Sulphites.

2. Phosphites.

b. Acids totally dissipated, leaving the base and charcoal.

\* Phosphate of ammonia is decomposed by heat and combustibles.

† The nitrate and hyperoxymuriate of ammonia are combustible alone. They disappear completely when heated.

; The genera in italics are placed from analogy only.

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### SECONDARY COMPOUNDS.

# +Acids partly sublimed unaltered.

1. Acetates.

2. Succinates.

3. Moroxylates.

4. Benzoates.

5. Camphorates.

++Acids wholly decomposed.

6 Oxalates.

7. Mellates.

8. Tartrates.

9. Citrates.

10. Kinates.

11. Saccolates.

12. Urates.

13. Sebates.

14. Malates.

15. Formiates.

16. Suberates.

+++Anomalous.

17. Gallates.

18. Prussiates.

Let us take a view of all these genera, following the order of the Table.

As the salts constitute a class of bodies of great importance to the practical chemist, but so numerous that it is difficult to remember the properties of each, it is of some importance to facilitate the means of comparing them together as much as possible. It will contribute considerably to this if the salts belonging to each genus be described exactly in the same order. This shall be attended to as much as possible in the following account of the salts.

The importance of the salts as chemical instruments

is very much connected with their solubility in water. Some are insoluble in that liquid, others dissolve in it with more or less facility. I shall lay hold of this circumstance to subdivide each genus into two parts : the first shall contain the salts which dissolve in water ; the second those which are insoluble. Many of the salts have not yet been applied to any useful purpose, while others are of importance either to the chemist or for the purposes of civilized society. After having described the properties of the salts belonging to each genus, I shall add a third part, in which some of the most important uses of the salts shall be mentioned. It will not be expected that I shall indulge in minute details, or attempt to exhaust so fertile a subject. Each genus, then, as far as possible, will be divided into three parts; namely, 1. Soluble salts; 2. Insoluble salts; 3. Uses of the salts of the genus described.

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# ORDER I.

# INCOMBUSTIBLE SALTS.

GENUS I. MURIATES.

THE muriates are the salts which have been longest known, and from which indeed the whole of the class have borrowed their name; for to them belongs common salt, the most important and the most indispensibly necessary of all the salts. They may be distinguished by the following properties:

Characters.

1. When heated, they melt, and are volatilized, at least in part, without undergoing decomposition. The first portions which fly off contain an excess of acid.

2. Not in the least altered by combustibles, even when assisted by heat.

3. Soluble in water. For the most part they raise the boiling point of water.

4. Effervesce with sulphuric acid, and white acrid fumes of muriatic acid are disengaged.

5. When mixed with nitric acid, they exhale the odour of oxymuriatic acid.

The alkaline and earthy muriates at present known amount to twelve.

I. SOLUBLE MURIATES.

# Sp. 1. Muriate of Potash.

THIS salt was formerly called *febrifuge* or *digestive* salt of Silvius, and regenerated sea salt.

#### MURIATES.

It may be prepared by dissolving potash in muriatic Chap. III. acid, and evaporating the solution till the salt crystallizes; but it is commonly obtained during other chemical processes.

Its crystals are cubes, but often rather irregular.

It has a disagreeable bitter taste. Its specific gravity is 1.836 \*.

When boiled in water, it dissolves in 1.7 times its weight of that liquid +. It requires three parts of cold water 1; but this difference is not sufficient to enable us to obtain regular crystals by allowing a saturated boiling solution of this salt to cool. Regular crystals can only be obtained by abandoning the solution to spontaneous evaporation.

It suffers little alteration from exposure to the air.

When exposed to heat, it decrepitates, melts when heated to redness, and at last is volatilized in a white smoke, but without decomposition. In a red heat it loses 2.86 per cent. of its weight ||.

It is not sensibly soluble in pure alcohol.

Many different analyses of this salt have been published, but they by no means agree with one another. The following Table exhibits the constituents according to the respective analists.

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\* Kirwan.

1 Bergman, Opusc. i. 134.

+ Wenzel's Verwandtschaft, p. 310. || Wenzel, Ibid. p. 312-

a the way that about a marked at a marked a

· Mathies, Malerice, Di (23).

Properties.

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\* + 11 1 t ş Acid. 21 29 31 34 .35 36 Base. 74 66 65 63 61 64 Water. 5 S 8 100 Total. 100 100 100 100 100

Composi-

tion.

These results appear altogether irreconcileable with each other; but the differences are rather apparent than real. The quantity of muriatic acid was estimated by precipitating it by means of nitrate of silver, and weighing the muriate of silver obtained. Now Bucholz formed his estimate by supposing that 100 parts muriate of silver contain only 11.5 muriatic acid, whereas they seem in reality to contain 18. Had he used the true proportion, the quantity of acid instead of 21 would have been 33. The water was estimated by exposing the salt to a red heat; now in this temperature, some of the acid probably escapes as well as the water. Upon the whole, the estimate of Wenzel appears to me to be the nearest to accuracy.

# Sp. 2. Muriate of Soda.

History.

THIS salt has been known and in common use as a seasoner of food from the earliest ages. It is known by

- \* Bucholz, Beitrage, iii. 133. + W
  - + Wiegleb, Ibid.
- t Bergman, Opuse. i. 134. § Rose, Gehlen's Jour. vi. 31. Wenzel. Verwandtschaft, p. 100. The water is supposed expelled.
- Kirwan, Nicholson's Quarto Jour. iii. 215.

#### MURTATES.

the names of common or sea salt ; sometimes it is called sal gem. In this country the term salt is usually applied to it without any addition. The nature of its acid was discovered by Glauber, if it was not known earlier. Stahl affirms in his Specimen Beccherianum, that its base is an alkali; but Duhamel was the first who showed how to obtain that base in a separate state, and who demonstrated the difference between it and potash.

This salt exists in great abundance native, and therefore is never formed artificially by chemists. Immense masses of it are found in different countries, which require only to be dug out and reduced to powder. In that state it is called rock salt. The water of the ocean also contains a great proportion of this salt, to which indeed it owes its taste, and the power which it possesses of resisting freezing till cooled down to 28.5%. When this water is evaporated sufficiently, the salt precipitates in crystals. It is by this process that it is obtained in this country. But the salt of commerce is not sufficiently pure for the purposes of chemistry, as it contains usually muriate of magnesia, &c.; but it may be obtained pure either by repeated crystallizations, or by the following process: Dissolve it in four times its weight of pure water, and filter the solution. Drop into it a solution, first of muriate of barytes, then of carbonate of soda, as long as any precipitate continues to fall. Separate the precipitates by filtration, and evaporate slowly till the salt crystallizes.

Muriate of soda usually crystallizes in cubes, which, Properties. according to Hauy \*, is the primitive form of its crys-

Chap. III.

\* Mineralogy, ii. 357.

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Book II. Division III. tals and of its integrant particles. Sometimes the angles of the cubes are truncated; and in urine the crystals of common salt, as Fourcroy and Vauquelin have ascertained, assume the form of octahedrons.

Its taste is universally known, and is what is strictly speaking denominated *salt*. Its specific gravity is 2·125\*. According to Bergman, it is soluble in 2·82 times its weight of cold water, and in 2·76 times its weight of boiling water +. When it is boiled for some time in water, it dissolves in 2·59 times its weight of that liquid ‡. The specific gravity of the saturated solution is 1·198, temperature 42°§. Pure alcohol does not dissolve this salt, but it is somewhat soluble in alcohol of .830.

It is not affected by exposure to dry air. The muriate of soda of commerce, indeed, contains a quantity of muriate of magnesia, which renders it deliquescent. It contains also sulphate of magnesia and sulphate of lime.

When heated, it decrepitates. In a red heat it melts and evaporates in a white smoke without undergoing decomposition. In a red heat it loses about 2 per cent. of its weight  $\|$ . Part of this loss is to be ascribed to the muriatic acid  $\P$ .

The following Table exhibits the result of the various analyses that have been made to ascertain the proportion of the constituents of this salt.

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Por LI.

\* Fahrenheit, Phil. Trans. 1724, vol. xxxiii. 114. Kirwan makes it 2·120, and Dr Watson found it 2·143. See his Essays, v. 67.

- + Opuse i. 134. t Wenzel's Verwandtschaft, p. 310.
- § Watson's Chem. Essavs, v. 85. [] Wenzel, Ibid. p. 312.
- ¶ Seignette, Baumé's Chimie, ii. 48.

#### MURIATES.

+ 8 1 1 Acid 28 43.20 4.4. 38.88 40 46 52 Base 58 56.80 54 50 66 53.00 42 Water 6 8.12 2 6 6 Total 100 100 100 100 100 100 100

The small proportion of acid obtained by Bucholz is to be ascribed to his mode of estimating the constituents of muriate of silver. When corrected it would become 44.3, which approaches the result obtained by Rose; and as it is nearly a mean of the analyses of Kirwan and Bergman, is probably very near the truth. The last column, then, founded on this result, is an approximation to the constituents of muriate of soda.

# Sp. 3. Muriate of Ammonia.

THIS salt was known to the ancients, and was called by them *sal ammoniac*, because it was found in great quantities near the temple of Jupiter Ammon in Africa \*\*. Its composition was first pointed out by Geoffroy junior in 1716 and 1723 ††, and afterwards more precisely by Duhamel in 1735 ‡‡. For many years the whole of the sal ammoniac used in Europe was im-

And strange of some of the

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History.

<sup>\*</sup> Bucholz, Beitrage, iii. 138.

<sup>†</sup> Kirwan, Nicholson's Quarto Jour. iii. 215.
‡ Wiegleb, Bucholz, Ibid.
§ Rose, Gehlen's Jour. vi. 32.
# Wenzel, Verwandtschaft, p. 101.
¶ Bergman, Opusc. i. 134.
\*\* Pliny, lib. xxxi. c. 7.
† Mem. Par.
‡ Ibid.

Book II. Division III. Properties.

I. ported from Egypt; but it is now made in great abun-III. dance both in Britain and on the continent.

Sal ammoniac is usually in the form of a hard elastic cake; but by solution in water and proper evaporation it may be obtained in crystals. The primitive form of these crystals is, according to Hauy, the octahedron; and that of its integrant particles the tetrahedron \* ... But it crystallizes most frequently in long four-sided pyramids. It often assumes the form of plumose crystals; the individual crystals of which arelong hexahedral pyramids.

The specific gravity of this salt, according to the experiments of Dr Watson, is 1.450<sup>+</sup>. A saturated solution of it in water at  $42^{\circ}$  is of the density 1.072.

In its ordinary compact state sal ammoniac is soluble in 3.25 times its weight of cold water  $\ddagger$ ; but the crystals, according to Gren, dissolve at the temperature of 50° in 2.727 parts of water §. Wenzel found it soluble in 2.24 parts of water of the temperature 144 5° ||. A hundred parts of alcohol of the strength 0.834 dissolve  $1\frac{1}{2}$  of this salt.

In its common form (which is an opaque mass) this salt is not much affected by the air, but its crystals are liable to deliquesce.

When heated, it sublimes without decomposition in the form of a white smoke, which exhales a pecular odour.

\* Hauy's Mineralogie, ii. 380.

+ Essays, v. 67. Wallerius makes it 1.453 (Chemistry, i. 266); and Kirwan, 1.420.

\* Wallerius' Chemistry, i. p. 256.

§ Gren's Handouch, i. 488.

Verwandtschaft, p. 309 .-.

When this salt is sublimed with gold leaf, there is found in the neck of the retort an amethyst-coloured matter, bordering on purple, soluble in water, and forming a purple solution. When filtered, there remains behind a purple powder. This salt seems from this to be capable of oxidizing gold \*.

The constituents of this salt seem first to have been discovered by Tournefort in 1700; but he did not succeed in ascertaining their proportion. The result of the different experiments made for this last purpose is as follows:

dine In:	+	4	\$	1	I.I.I	100 000
Acid	31	40	42.75	49	76-3	48.
Base	69	6.0	25:00	51	23.7	14.9
Water			32:25	2	* 142 J	37.1
Total	100	100	100	100	100	100

The low estimate of acid in the analysis of Bucholz depends, as has been already observed, upon h statement of the proportion of acid in muriate of silver. When corrected, the true number turns out 48 which

\*Storr, Crell's New Discoveries. &c. Part ii. p. 41.

+ Bucholz, Beitrage, iii. 146. ‡ Wiegleb, Ibid.

§ Kirwan, Nicholson's Quarto Jour. iii. 216.

|| Wenzel's Verzvandtschaft, p. 102.

¶ This is not the result of an analysis, but of a calculation founded on the supposition, that equal bulks of ammoniacal and muriatic acid gas condense each other; which is not far from the truth. In the first and second analyses the water is included in the proportion of base stated.

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Book II. Division III. comes very near the estimate of Wenzel. If the estimate stated in the sixth column of the preceding Table be nearly correct, as is to be presumed, then the water in 100 parts of sal ammoniac must amount to 37.1. From these data, the numbers in the last column of the Table were obtained, which exhibit an approximation to the true proportions of the constituents of this salt. Variations in the proportion of the water, which may be expected in different samples, will account for the discordance in the different analyses exhibited above.

# Sp. 4. Muriate of Magnesia.

History. THIS salt exists in sea-water, and in several mineral springs, particularly that at Lymington in Hampshire. It was first described by Mr Brown in the Philosophical Transactions for 1723 \*; but its composition was not understood till long after, when the experiments of Black and Margraf had established the peculiar nature of its base. Bergman afterwards published a description of it  $\dagger$ .

As it is found native in abundance, it is seldom formed artificially; but it may be prepared by dissolving carbonate of magnesia in muriatic acid, and evaporating the solution to a proper consistency.

Properties.

It is not easily crystallized. Bergman's method was to evaporate it by a considerable heat to the proper degree of concentration, and then to expose it to a sudden cold. By this method he obtained it in small needles ‡. Its specific gravity is 1.601 §.

\* Phil. Trans. xxxii. 348. ‡ Bergman, i. 382. \$ Hassenfratz, Ann. de Chim. xxviii. 12.

#### MURIATES.

Its taste is extremely bitter, hot and biting. It requires rather more than half its weight of water to dissolve it; for when exposed to the air it runs into a liquid, and attracts  $\frac{66}{100}$  parts of its weight of water\*. The solubility in alcohol increases with the strength of that liquid. Alcohol of .817 dissolves half its weight of it, but alcohol of .900 only  $\frac{1}{2}$ th of its weight  $\frac{1}{2}$ .

A saturated solution of it quickly forms a jelly; on which, if hot water be poured, spongy masses are formed, not even soluble in muriatic acid ‡.

It deliquesces very speedily when exposed to the air.

A strong heat decomposes it completely, according to Fourcroy. When dried in a high temperature, it is very caustic §.

The following Table exhibits the proportions of its constituents, according to the experiments of different chemists:

Saving 740	1	T	**	
Acid	34	34.59	57	
Base	41	31.07	43	
Water	25	34.34		
Total	100	100 .	100	

Composi-

\* Bergman, Opusc. i. 136.

\$ Bergman, i. 382.

|| Bergman, Opusc'i. 136.

Kirwan on Mineral Waters, p. 294.
Westrumb, Ann. de Chim. ii. 135.
Kirwan, Nich. Quarto Jour. iii. 215.

\* \* Wenzel, Verwandtschaft, p. 104.

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Book H. D vision III. The estimate of Kirwan seems the most correct; that of Wenzel does not differ much; while Bergman, who appears to have inserted the water from calculation, has erred very considerably.

# Sp. 5. Muriate of Ammonia-and-Magnesia.

THIS salt was first mentioned by Bergman in 1775\*. It was afterwards described more particularly by Fourcroy in 1790 +.

It may be prepared by mixing together solutions of muriate of ammonia and muriate of magnesia, or by adding ammonia to the muriate of magnesia with excess of acid, and evaporating.

Properties.

Its crystals are so exceedingly small and irregular, that their figure has not been determined.

Its taste is bitter and ammoniacal. It is soluble in about six parts of cold water, and in a smaller proportion of boiling water. It is but little altered by exposure to the air. Heat decomposes it.

Composition. According to Fourcroy, it is composed of

27 muriate of ammonia

73 muriate of magnesia

100t

# Sp. 6. Muriate of Lime.

THIS salt has been long known to chemists. It was formerly called *fixed ammoniac*, because it was commonly obtained by decomposing sal ammoniac by means of lime.

> \* Opusc. i. 370. † Fourcroy, iii. 370.

+ Ann. de Chim. iv. 222.

#### MERIATES.

It is usually prepared from the residue of that process, but it may be obtained by dissolving carbonate of lime in muriatic acid.

Its crystals are six-sided striated prisms, terminated Properties. by very sharp pyramids. It is not easy to procure it in crystals, in consequence of its extreme tendency to deliquesce. Indeed, in summer, it is next to impossible to procure good crystals; but in winter they form spontaneously, if we dissolve four parts of the salt in one of water, of the temperature of 70°, and expose the solution in an atmosphere of 32°.

The taste of this salt is very bitter and pungent. Its specific gravity is 1.76 \*.

It is extremely soluble in water; water at 60° dissolving very nearly four times its weight of it. The solubility diminishes very rapidly with the temperature. Hence water at 30° does not dissolve above half that quantity, while at 100° it dissolves any quantity of it whatever. In hot weather, therefore, it cannot be obtained in crystals, but only in a hard, white, solid mass.

Mr Walker has ascertained, that when the evaporation of the solution is carried on till its specific gravity is 1.450 at the temperature of 80°, it crystallizes when exposed to an atmosphere whose temperature When its specific gravity at 80° is 1.490, is 32°. it assumes on cooling the form of a hard pearl-coloured mass +.

Alcohol dissolves this salt so copiously when concentrated, that I presume it is capable of taking up considerably more than its own weight of the salt, even

\* Hassenfratz, Ann. de Chim. XXVIII. 12.

+ Nicholson's Journal, v. 226.

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Book II. Division III. though previously exposed to a red heat to dissipate the moisture. So much heat is evolved during the solution as to cause the alcohol to boil.

When this salt is exposed to the air, it attracts moisture very speedily, and deliquesces.

When exposed to the action of heat, it swells up, melts, and then loses its water of crystallization. A violent heat separates a small portion of its acid. When thus reduced to a submuriate, it has the property of shining in the dark, as Homberg first observed: Hence it has been called the *phosphorus of Homberg*.

The following Table exhibits the result of the different experiments made to ascertain the constituents of this salt, not in the state of crystals, but reduced by heat to a dry mass.

Composition,

	*	+	\$
Acid	31	42	51
Base	44	50	19
Water	25	8	
Total	100	100	100

These analyses differ very much from each other; that of Kirwan is nearest the mean, and is probably the most correct.

\* Bergman, i. 136. The salt was well dried.

+ Kirwan, Nicholson's Q. rto Jour. iii. 215. The salt had been exposed to a red heat before analysis.

\$ Wenzel, Verwandtschaft, p. 1.3.

#### MURIATES.

# Sp. 7. Muriate of Barytes.

THE properties of this salt were first investigated by Scheele \*. Dr Crawford wrote a treatise on it in 1790. Since that period many processes have been published for preparing it +. To Kirwan, Hauy, Bucholz, and Bouillon La Grange, we are indebted for most of the additions made to the description of this salt by Scheele.

The easiest method of preparing it would be to dissolve carbonate of barytes in water and crystallize the solution; but as the carbonate of this earth is rare, the salt is usually formed by calcining in a crucible a mixture of sulphate of barytes and charcoal, decomposing by means of muriatic acid the sulphuret formed, filtrating the solution, evaporating it till a pellicle begins to form on its surface, then allowing it to cool slowly. The crystals of muriate of barytes gradually deposite. If the salt happens to be contaminated with iron, which is often the case, the crystals are to be calcined, dissolved in water, the solution filtered and crystallized again. By this process the oxide of iron is separated. The improvements proposed lately consist in promoting the fusion and decomposition of the sulphate of barytes, by adding to the mixture sulphur, muriate of lime, or common salt.

The primitive form of muriate of barytes is, accord- Properties. ing to Hauy, a four-sided prism, whose bases are squares. Its integrant particles have the same figure ‡.

+ See Van Mons, Jour. de Phys. xlv. 297. Goettling, Phil. Mag. xxii. 218. Bouillon La Grange, Ann. de Chien. xlvii. 139. Resat, Ibid. lv. 51. ‡ Fourcroy, iii. 232. English Trans.

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Prepara. tion.

<sup>\*</sup> Crell's Annals, iii. 6. English Translation.

Book II. Division III. It crystallizes most commonly in tables. Sometimes it assumes the form of two eight-sided pyramids applied base to base \*.

It has a pungent and very disagreeable taste; and, like all the other preparations of barytes, is poisonous. Its specific gravity is 2.8257<sup>+</sup>.

It requires 2.29 parts of water, of the temperature 190°, to dissolve one of this salt. It is scarcely less soluble in cold water. Hence it cannot be procured in crystals by cooling a saturated solution of it in hot water  $\ddagger$ .

From the experiments of Bucholz we learn, that pure alcohol while cold dissolves no sensible portion of it; but at a boiling heat it is soluble in 400 parts of that liquid §. Weak alcohol dissolves a little of it, and the solubility increases with the dilution. Alcohol of  $\cdot$ 900, for instance, dissolves  $\frac{1}{100}$  of its weight of this salt ||.

It is not altered by exposure to the open air. When heated, it decrepitates and dries, and when the temperature is very high it melts; but no heat which we can apply is capable of decomposing it.

The following Table exhibits the experiments made by chemists to ascertain the proportion of its constituents.

\* Crawford.

t Crawford.

§ Beitrage, iii. 2.4.

Kirwan, on Mineral Waters, p. 274.

<sup>+</sup> Hassenfratz, Ann. de Chim. xxviii. 12.

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	*	+	****	1
Acid	20	22.93	23.8	24
Base	64	62.47	76.2	60
Water	16	14.60	i soffer	16
Total	100	100.00	100	100

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Composi-

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These analyses agree nearly with each other. Mr Kirwan's, from the great care with which it was made, seems entitled to the most confidence.

# Sp. 8. Muriate of Strontian.

THIS salt was first described by Dr Crawford in 1790. It was afterwards examined by Dr Hope, by Klaproth, Pelletier, Fourcroy, and Vauquelin.

It may be prepared by dissolving carbonate of strontian in muriatic acid, or by decomposing sulphuret of strontian by means of that acid. The solution is then to be evaporated to a proper consistence, in order to obtain the muriate in crystals.

Its crystals, according to Hauy, are very long, slen- Properties. der, hexagonal prisms §. It has a peculiar sharp, penetrating taste. Its specific gravity is 1.4402 ||.

Three parts of these crystals are soluble in two parts of water at the tempereture of  $60^\circ$ . Boiling water dissolves any quantity of them whatever ¶. From the ex-

\* Kirwan, Nicholson's Quarto Journal, iii. 25. The salt in the second column was in crystals, in the fourto dried.

- + Aiken, Nicholson's Jour. xxii. 301.
- ‡ Fourcroy, iii. 236. Engl. Trans. § Ib. 262.
- Hassenfratz, Ann. de Chim. xxviii. 12.

According to Crawford, they dissolve in 0.825 of water of the tem-

Book II. Division III. periments of Bucholz, we learn that 24 parts of pure alcohol, at the temperature of 60°, dissolve one part of this salt; and that it is soluble in 19 parts of pure boiling alcohol \*. The alcohol solution burns with a fine purple colour.

The crystal suffers no change when exposed to the air, except it be very moist; in which case they deliquesce.

When heated, they first undergo the watery fusion, and are then reduced to a white powder. A very violent heat is said to decompose this salt.

Muriatic acid precipitates this salt from its solution in water +. Hence it crystallizes most readily when there is an excess of acid in the solution.

The constituents of this salt, according to the analyses hitherto given, are as follows :

<u> </u>	1	\$	+	ion in start [10 -	1
Acid	18	23.6	31	38.33	3
Base	40	36.4	69	61.67	
Water	42	40		ut Lougherest visit	2
Total	100	100	100	100.00	Ę

Sp. 9. Muriate of Alumina.

THIS salt was first described by Margraf in his dissertation on the *Earth of Alum*, published in the Berlin

perature 190°; but they are much less soluble in cold water. Hence they crystallize in cooling.

+ Hope.

1 as gridtaith a

- \* Bucholz' Beitrage, iii. 29.
- ‡ Kirwan, Nicholson's Quarto Jour. iii. 215.
- § Vauquelin, Fourcroy, iii. 265. Engl. Trans.
- Rose, Gehlen's Jour. vie 33.

Composi-

History.

Memoirs for 1754\*. Scarcely any addition has been made to the facts which he ascertained, except by Bucholz + and Wenzel ‡.

It is prepared by dissolving alumina in muriatic acid: It is always in the state of a supermuriate.

It is scarcely possible to obtain it in the form of cry- Properties. stals: it is usually either gelatinous, or in the state of white powder.

It is extremely soluble in water, one part of that liquid being sufficient to reduce four parts of the dry salt to the consistence of a syrup §. When exposed to the air, it speedily deliquesces into a liquor of a glutinous consistence.

Pure alcohol, in the mean temperature of the atmosphere, dissolves half its weight of this salt; and when boiling, it takes up at least two-thirds of its weight, but deposits again a part as the solution cools  $\P$ .

When heated, it melts and loses its acid, while the alumina remains behind in a state of purity ||.

Its constituents, according to the analyses hitherto made, are as follows:

d types	**	* *	††
Acid	19	29.8	27:7
Base	30	30.0	72.3
Water	51	40.2	(SYB M)
Total	100	100	100

\* Margraf's Opusc. ii. 118. † Verwandtschaft, p. 111. + Beitrage, iii. 109.

§ Bucholz, Ibid. p. 115.

¶ Margiaf, Ibid.

|| Ibid. p. 111.

\*\* Bucholz, Ibid. The second column contains his analysis as he

Composition.

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Book II. Division III. These analyses are altogether irreconcileable, unless we suppose that Wenzel's earth was impure, and that it was not dried sufficiently.

# Sp. 10. Muriate of Yttria.

THIS salt has been examined by Eckeberg \*, Vauquelin †, and Klaproth ‡. It has a strong resemblance to the nitrate of yttria. Like that salt, it dries with difficulty, melts in a gentle heat, and attracts moisture very rapidly from the atmosphere. It does not crystallize, but runs into a jelly.

# Sp. 11. Muriate of Glucina.

THIS salt has only been examined by Vauquelin; and little more known at present concerning its properties than that it resembles nitrate of glucina, but is more easily crystallized. When dissolved in weak alcohol, it forms an agreeable sweet liquid.

### Sp. 12. Muriate of Zirconia.

Properties.

This salt was first examined by Klaproth : It was afterwards described more particularly by Vauquelin.

It is easily formed by pouring muriatic acid on newly precipitated zirconia. It is colourless; its taste is very astringent; by evaporation it furnishes small transparent crystals in needles, which lose their transparency in the air. Muriate of zirconia is very soluble in wa-

transferration and an and a

states it; the third the same analysis, altering the proportion of acid to that which would have resulted from supposing muriate of silver to contain eighteen *per cent*, of acid.

- tt Wenzel, p. 112.
- + Ann. de Chim. XXXVI. 157.
- \* Crell's Annals, 1799, ii. 70.
- \$ Beitrage, iii. 69.

ter and in alcohol; to the flame of which it does not communicate any particular colour. Heat decomposes it; and it is decomposed likewise by the saliva when taken into the mouth.

When muriate of zirconia contains a little silica, it forms cubic crystals without consistence, and resembling a jelly. These crystals, when exposed to the air, gradually lose their transparency, and diminish in volume; and there are formed in the middle of the salt white silky needle-shaped crystals.

Muriate of zirconia is decomposed by sulphuric acid; part of the sulphate precipitates, and part remains dissolved in the muriatic acid. When this acid is driven off by heat, the remainder of the sulphate is gradually deposited : if the evaporation be stopped before the mass be reduced to dryness, it forms a kind of jelly when cold. It is also decomposed by the phosphoric, citric, tartaric, oxalic, and saclactic acids, which form with zirconia insoluble compounds that precipitate in white flakes.

The gallic acid poured into muriate of zirconia produces a white precipitate; but a green, bordering on grey, if the zirconia contains iron ; and this last precipitate becomes, when dry, of a bright black colour, and resembles China ink. The liquid preserves & greenish colour : new portions of gallic acid produce no farther precipitation; but carbonate of ammonia separates in great abundance a flaky matter of a purplish colour. not unlike that of the leys of wine. From these experiments it follows, that gallic acid has a greater affinity for zirconia than muriatic acid has; and that the gallates of zirconia and iron are soluble in muriatic acid. Pp Qq

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Action of gailic acid.

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Book II. Division III. Carbonate of potash decomposes muriate of zirconia, and part of the carbonic acid combines with the earth, and renders it easily soluble in acids though dried.

Carbonate of ammonia occasions a precipitate, which is mostly dissolved by adding more carbonate.

Prussiate of mercury produces an abundant precipitate, which is soluble in muriatic acid; and which consequently is not muriate of mercury.

A plate of zinc, introduced into a solution of muriate of zirconia, occasions a slight effervescence; the liquor becomes milky, and in a few days assumes the form of a white semitransparent jelly.

Alumina decomposes muriate of zirconia with the assistance of a slight heat; the alumina dissolves, the liquor becomes milky, and assumes the form of a jelly. When the muriate contains iron, it remains in the solution, and the precipitated zirconia is quite pure. Here, then, is a method of freeing zirconia from iron \*.

H. INSOLU-BLE MURI-ATES.

<sup>5</sup> SUCH are the properties of those muriates that are soluble in water. No alkaline or earthy muriate is at present known that is insoluble in that liquid; of course the second division of this genus does not exist.

THE following Table exhibits the solubility of the muriates in water and in alcohol, and the proportion of the constituents of each, selected from the analysis that seems best entitled to confidence.

\* Vauquelin, Ann. de Chim. xxii. 201.

MURIATES.

1	Solubility Solubility Strength			Constituents.			
Muriates of		in 100. Alcohol.	of Alcohol.	Acid.	121-1-1-1-1	Water.	
Ammonia	30.77	1.5	•834	100	33	78	
Magnesia	151	50.0	•817	100	89.8	99•3	
Soda	35.46	0.2	•834	100	114	14	
Lime	400	100+x	•800	100	118.3	TEN B	
Potash	33	0.38	•834	100	185.7	a war	
Strontian	150	4.16	•796	100	216.2	233	
Barytes	43	0.00	•796	100	314.5	87	
Alumina	400	50	•796	100	100	135	
Yttria	is die bi	1 (J.M.)	adirecto	- 22	the ghity	tindy it.	
Glucina	and the second				ni 4sthi	1000 C	
Zirconia	litur og	a farma (	to buy	ill, in	nia one	iquit 13	

Chap. III.

Solubility and constituents of muriates.

OF the 12 salts described above, there are only five or six that have been hitherto applied to any useful purpose. The following are the most important.

1. Muriate of potash. This salt is employed by the alum-makers to procure the crystallization of alum, and is prepared from the waste leys of the soap-makers for that purpose.

II. Muriate of soda. This is without doubt the most valuable of all the salts; the uses to which it is applied are too numerous to be detailed here, and, besides, they are very generally known.

III. USES OF THE MURI-ATES. Book II. Division III.

As a seasoner of food it seems to be almost essential to health. The inhabitants of maritime districts are too easily supplied with it to be sensible of its value; but the case is very different in those countries that are at a distance from the ocean. Wherever it is found in the soil of the inland parts of America, thither the wild beasts resort in multitudes. They apply their tongues to the impregnated earth, and gather as much as will satisfy their wants. These places are called *licks* by the Anglo-Americans. So eager are these animals to obtain salt, that they will suffer themselves to be caught rather than leave the spot \*.

It is needless to mention the great consumption of salt in order to preserve animal food from putrefaction; the application of it to the glazing of pottery, and to the preparation of leather; the use of it in metallurgy, in purifying oils, in soap-making, and a hundred other arts.

Methods of extricating soda from it. Its utility in chemistry is equally extensive. From it alone are muriatic and oxymuriatic acids obtained; and from it also, of late, great quantities of soda have been extracted, and introduced with advantage as a substitute for the soda formerly obtained from the combustion of vegetables.

The acid is easily extracted from this salt by means of sulphuric acid: But to obtain the alkali at a cheap rate is not so easy. The methods which have hitherto succeeded may be reduced to two.

1. Muriate of soda is decomposed by means of some substance which has a stronger affinity for muriatic

\* See Phil. Mag. xx. 97.

#### MURIATES.

acid than soda has. The soda by this process is set at , Chap. III. liberty, and may be obtained by evaporation and crystallization. Barytes and potash would answer this purpose completely; but unluckily these bodies cannot be obtained sufficiently pure, except at an expence which precludes their employment. There are, however, three substances, which are also capable of setting the base of common salt at liberty, and of furnishing soda, either pure or in the state of carbonate. These are litharge, lime, and iron.

When about four parts of litharge and one of com- I. By limon salt, properly pounded and mixed, are macerated in a little water for several hours, and stirred repeatedly, the muriatic acid gradually combines with the oxide of lead, and forms a muriate, while the soda is left in solution, and may be obtained separately by filtration and evaporation. The decomposition goes on still more rapidly if the mixture be heated during the process.

The fact, that the red oxide of lead decomposes muriate of soda, which was first observed by Scheele, has given occasion to much speculation among chemists. Mr Hassenfratz endeavoured to account for it, by supposing that the oxide is combined with carbonic acid, and that therefore it is a case of compound affinity. Mr Curaudau has proved that carbonic acid, instead of promoting, impedes the decomposition ; and that, in fact. carbonate of lead is incapable of decomposing muriate of soda. He concludes, therefore, that the phenomenon cannot be accounted for by the commonly received laws of affinity \*. Vauquelin has proved more lately, that

\* Ann. de Chim. xiv. 15.

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tharge,

Book II. Division III. the decomposition by means of litharge is complete, provided the quantity of that oxide be greater than that of common salt; that the resulting compound is a submuriate of lead totally insoluble in water, and which is not decomposed by alkalies. Hence he ascribes the decomposition to the attraction of muriate of lead for an excess of oxide \*. But this does not account completely for the decomposition, provided it be true that oxide of lead has a weaker affinity for muriatic acid than soda has. Berthollet has at last explained this apparent anomaly by proving, that when two substances are mixed with a third, for which each has an affinity, they divide it between them in proportions corresponding to the quantity of each : And if the compound formed by one of these substances with the third be insoluble, that substance combines with the whole of the third body, and takes it completely from the other; because the insoluble compound being in fact totally abstracted from the mixture, the decomposition and partition commences again as at first after every partition. Thus when the oxide of lead and muriate of soda are mixed together, the oxide and alkali divide the muriatic acid between them, so that some of the common salt is decomposed, and some muriate of lead formed immediately after the mixture. But this being in the state of submuriate, or altogether insoluble, separates completely from the rest: in consequence of which a new partition of the muriatic acid between the oxide and the alkali takes place; and this continues, provided the quantity of litharge be sufficient, till the common salt is entirely decomposed.

\* Ann. de Chim. xxxi. 3.

#### MURIATES.

That the alkali may be extracted from common salt Chap. III. by means of lime, may be considered as a fact for which 2. By lime, likewise we are indebted to Scheele. Cahausen indeed had hinted at it in 1717; but his treatise had been forgotten \*. Scheele ascertained that a mixture of lime and common salt, formed into a paste, and placed in a moist cellar, was covered with an efflorescence of soda in 15 days +. In 1782 Morveau and Carny procured a patent from the French government to establish a manufactory at Croisic for extracting soda from common salt by means of lime. These process was exactly the same with that of Scheele, only upon a larger scale. It does not appear, however, that the manufactory was ever established. Berthollet has rendered it probable that the soda which is found abundantly on the west of Egypt, is formed naturally by a similar process 1.

To Scheele likewise we are indebted for the disco- 3. By iron, very that common salt may be decomposed by iron. He observed that a wooden vessel placed in a cellar, and containing brine, had its iron hoops covered with an efflorescence of soda. This induced him to dip a plate of iron into a solution of common salt, and to suspend it in a cellar. After an interval of fourteen days, he found his iron incrusted with soda §. The same decomposition takes place also if zinc or copper be substituted for iron ||.

2. The second method of extracting soda from common salt is less direct. It consists in displacing the muriatic acid by means of some other acid, which may

- \* See his Helmontins Extaticus. \$ Ann. de Chim. xxxiii. 345. | Athenas, Ann. de Chim. xix. 92.
- + Scheele, ii. 15.
- § Scheele, ii. 14.

Book II. Division I I.

be afterwards easily decomposed or displaced in its turn thus the soda is left behind at last in a state of purity. The acids which have been made choice of are the sulphuric and the acetic; the boracic, phosphoric, and arsenic acids might indeed be employed, as they decompose common salt in a high temperature. The products in that case would be borate of soda, or the phosphate, or arseniate, of the same base, according to the acid. These salts might be afterwards decomposed by means of lime, and the soda obtained separate. But these acids are a great deat too high priced to admit of their employment.

4. By sulphuric acid and its compounds.

Sulphuric acid may be either employed in a separate state, or in combination with bases, when the salts which it then forms can be procured at a sufficiently cheap rate. Alum, sulphate of lime, and sulphate of iron, have been respectively employed with advantage to decompose common salt, and obtain sulphate of soda. Alum is said to have been first employed for that purpose by Constantini, a physician of Melle, near Osnaburg, about 1750. The process, it is affirmed, does not succeed except at a low temperature\*. Sulphate of lime decomposes common salt when formed with it into balls, and exposed to a strong heat +. Much discussion has taken place among the German chemists about the possibility of decomposing common salt by means of sulphate of iron. That sulphate of soda may be obtained by exposing a mixture of these two salts to a strong heat, was first announced by Vander Ballen. This was contradicted by Hahneman, but confirmed by

<sup>\*</sup> Jour. de Min. No. iii. p. 55.

<sup>+</sup> Malherbe and Athenas, Ann. de Chim. xix.

the experiments of Tuhten\*, Lieblein+, and Wiegleb t. It succeeded completely with the French commissioners. Lelievre, Pelletier, Darcet, and Giroud, who were appointed in 1794 to examine the different processes for obtaining soda from common salt. They ascertained also that pyrites or supersulphuret of iron may be employed for the same purpose  $\S$ .

After obtaining the sulphate of soda, it is necessary to expel the acid in order to procure the soda separately. This is accomplished by calcining the salt mixed with a certain portion of charcoal or of pit-coal. By this process it is converted into sulphuret of soda, and the sulphur may be abstracted by the intervention of iron or chalk. When the sulphuret of soda is nearly in fusion, small bits of iron (the parings of tinplate answer best) are thrown in gradually in sufficient quantity to decompose the sulphuret. The fire is raised till the mixture melts. The sulphur, having a stronger affinity for the iron, combines with it and leaves the soda, which may be separated by solution in water, filtration. and evaporation ||. Carbonate of lime may be employed also for the same purpose ¶.

Some chemists have proposed to decompose common 5. By acesalt by means of acetate of lead, using either the acetate of commerce, or one formed on purpose, by combining litharge with the acid liquor obtained by distilling wood. The acetate of soda formed by mixing

tate of lead.

\* Crell's Annals, 1790. ii. 406.

‡ Ibid, 1793, i. 204.

+ Ibid. p. 509. § Ann. de Chim. xix. 58.

| Aiban, Ann. de Chim. xix. 77 .- The process was discovered by Malherbe. See Jour. de Min. No. ni. p. 67.

I Leblanc, Ann. de Chim. Kik. 61.

Chap. III.

Book II. Division III. common salt with these acetates is afterwards calcined, in order to decompose and expel the acetic acid. But these salts are too high priced to be employed with advantage to extract soda from common salt \*.

III. Muriate of Ammonia. This salt is in some degree combustible. Hence its importance to prevent the oxidizement of metals. For many years the whole of the sal ammoniac used in Europe was imported from Egypt. In that country the greater part of the fuel consists of the dung of their cattle formed into balls and dried. These excrementitious matters seem to contain muriate of soda, or rather muriate of ammonia ready formed; owing perhaps to the saline matters on which the animals feed. The soot formed during the combustion of this fuel is carefully collected and put into large glass bottles, which are exposed, in furnaces constructed on purpose, to a pretty strong heat. The sal ammoniac gradually sublimes, and attaches itself to the upper part of the bottles, where it forms a cake of some inches in diameter. Though this process was communicated to the Academy of Sciences in 1719 by Lemere. French consul at Cairo, it was a considerable time before the chemists in Europe thought of imitating it, or of preparing sal ammoniac themselves. The first manufactory in Germany was begun by Gravenhorst in 1759 +. Soon after it was made in France by Baumé. and in Scotland by Dr Hutton.

Preparatioa. The processes most commonly followed in Europe .

\* For a detailed account of the processes of making salt followed in different countries, the reader is referred to Brownrigg's Art of making Common Salt, and to Watson's Chemical Essays, ii. 33. † Wiegleb's Geschichte, ii. 55.

## MURIATES.

have been, 1. To form a sulphate of ammonia; to mix that salt with muriate of soda; and to expose the mixture to a beat sufficient to sublime the muriate of ammonia. The ammonia is usually obtained by the distillation of animal substances, or from soot. 2. To decompose muriate of lime by means of ammonia. 3. To combine muriatic acid directly with ammonia, and to sublime.

This salt is applied to a great variety of purposes. It is from it that pure ammonia is usually extracted. A considerable portion of sal ammoniac is consumed by coppersmiths, &c. who employ it to prevent the oxidizement of the surface of the metals which they are covering with tin. Dissolved in nitric acid, it forms aqua regia, employed in the solution of gold. It has ... the curious property of rendering many metallic oxides volatile, and is often used by metallurgists to separate metals from each other. These different metallic flowers, as they were called, or combinations of sal ammoniac with metallic oxides, were formerly used in medicine. Great quantities of this salt were once consumed by the dyers, though it is difficult in many cases to see for. what purpose. At present, much of the sal ammoniac made in this country is said to be exported to Russia.

IV. Muriate of Lime. This salt was proposed by Fourcroy as a remedy in scrofulous diseases; but it does not seem to have come into use in this country as a medicine. The discovery of Lowitz of the great cold which it generates when mixed with snow, has made it extremely useful as an ingredient in freezing mixtures. The same chemist has taught us the method of purifying alcohol and ether by means of it, from the water and alcohol with which they are respectively contaminated. 603

Chap. IIL

Book I'. Division III. V. Muriate of Barytes. This salt has been recommended as a cure for scrofulous disorders. The dose is from five to twenty drops or more. Care ought to be taken not to use it in too great quantities, as, like all other barytic salts, it is poisonous.

In chemistry it is much employed as a reactive to detect the presence of sulphuric acid. When dropt into a liquid holding that acid in solution, an insoluble precipitate of sulphate of barytes immediately appears. Bergman informs us that this precipitate is visible when the acid amounts only to 0.0002 of the liquid. Even when only 0.00009 of sulphuric acid is present, a slight cloud appears in a few minutes after dropping in the muriate \*.

The other muriates have scarcely been brought into common use either in chemistry or the arts.

## GENUS II. FLUATES.

THESE salts were first made known to the world by Scheele in 1771 +; and succeeding chemists have done little more than repeat and confirm his experiments.

C haracters.

Fluates may be distinguished by the following properties:

1. When sulphuric acid is poured upon them, they emit acrid vapours of fluoric acid, which have the property of corroding glass.

2. When heated, several of them phosphoresce.

3. Not decomposed by heat, nor altered by combustibles.

4. Combine readily with silica by means of heat.

\* Bergman, i. 100.

4 Scheele, i. 26.

#### FLUATES.

Most of them are but sparingly soluble in water; but their properties have been but imperfectly examined.

Sp. 1. Fluate of Potash.

THIS salt is most readily procured by fusing in a platinum crucible a mixture of fluor spar and carbonate of potash. The mass, digested in water, yields a solution, which, filtered and evaporated, leaves fluate of potash, It has scarcely been examined.

According to Scheele, it does not crystallize, but forms a gelatinous mass almost without taste, which attracts moisture from the air. It dissolves readily in water. When exposed to the fire it melts without any ebullition \*.

Wenzel says, that it forms crystals when free from all admixture of siliceous earth †.

## Sp. 1. Fluate of Potasb-and-Silica.

WHEN fluoric acid is obtained by the common process in glass vessels, it is always combined with a portion of silica. If into this impure acid a quantity of potash, or the carbonate, sulphate, nitrate, or muriate of that alkali, be dropt, a gelatinous precipitate immediately appears, which, when dried, becomes white like chalk, and separates into small loose grains like the sand of an hour-glass. This powder is a combination of fluoric acid, silica, and potash. Its nature was first ascertained by Scheele.

\* Scheele on Fluer, i. 26.

+ Gren's Hundbuch, i. 531.

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Chap. III.

I. SOLUBLE FLUATES.

Beok II. Divisien III. It has an acid taste, and is soluble in about 150 parts of boiling water; but is again partly deposited as the solution cools. When strongly heated, it melts into a transparent glass, and loses its acid \*.

Mr Scheele has shown, that a similar triple salt may be formed by using soda, or the salts containing soda, instead of potash.

Lime also is capable of combining with these triple salts, and forming with them quadruple salts, composed of fluoric acid, silica, fixed alkali, and lime †.

# Sp. 3. Fluate of Soda.

THIS salt may be formed as the fluate of potash. When the solution is evaporated till a pellicle forms on its surface, it yields on cooling small cubic crystals of fluate of soda. These crystals have a bitter and astringent taste; they do not deliquesce in the air, and are but sparingly soluble in water. Before the blow-pipe they decrepitate, and melt into a transparent globule  $\ddagger$ .

## Sp. 4. Fluate of Ammonia.

THIS salt may be obtained by applying a sufficient heat to a mixture of sulphate of ammonia and fluor spar. Fluate of ammonia sublimes; or it may be prepared by saturating fluoric acid with ammonia. The solution yields by evaporation small crystals of fluate of ammonia. When heated, it sublimes in the state of a superfluate.

\* Scheele, Crell's Annals, i. 214. Engl. Transl. + Ibid. 219. ‡ Fourcroy, iii. 306.

#### FLUATES.

## Sp. 5. Fluate of Alumina.

THIS salt does not crystallize; but assumes, when evaporated, the consistence of a jelly. Its taste is astringent, and it contains always an excess of acid.

THE FLUATES of yttria, glucina, and zirconia, have not been examined.

II. INSOLU-BLE FLU-ATES.

# Sp. 6. Fluate of Magnesia.

THIS salt may be formed by dissolving carbonate of magnesia in fluoric acid. The salt precipitates in a great measure as the saturation approaches.

It is not soluble in water except there be an excess of acid. In that case, by spontaneous evaporation, it forms hexagonal prisms, terminated by a low pyramid composed of three rhomboidal sides.

These crystals are hardly soluble in water. Alcohol dissolves a small portion of them. Heat does not decompose them; nor are they decomposed by any acid<sup>\*</sup>.

## Sp. 7. Fluate of Lime.

THIS salt exists abundantly native. It is from it indeed that fluoric acid is always extracted.

It is found frequently crystallized. The primitive form of its crystals, according to Hauy, is the octahedron, but it occurs more frequently in cubes; sometimes the angles, and sometimes the edges of these cubes, are truncated. The form of its integrant particles is the regular tetrahedron.

\* Bergman, i. 384.

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Book II. Division III.

Phospho-

Besces.

This salt has no taste. Its specific gravity is 3.15. It is insoluble in water, and not altered by exposure to the air.

When heated, it decrepitates and phosphoresces strongly in the dark. It emits this light even under water, or in the vacuum of an air pump. When kept hot for some time, it ceases to shine, and the phosphorescent property cannot be again restored to it, by any process known, except by decomposing it altogether by means of sulphuric acid, and forming it anew. Scheele ascertained that new-formed fluate of lime is equally phosphorescent with native. The cause of this curious property is not well understood. After being heated, the salt, though it refuses to phosphoresce any more, has not lost any perceptible weight, nor is it altered in any of its other qualities. When strongly heated, fluate According to of lime melts into a transparent glass. Saussure, this takes place at the temperature of 51° Wedgewood \*.

When heated with sulphuric, phosphoric, or arsenic acid, the fluoric acid is driven off in white fumes; but neither the nitric nor muriatic decompose it, according to the experiments of Scheele. The following Table exhibits its constituents according to the most accurate analysis hitherto made.

\* Jour. de Pbys. xlv. 16.

FLUATES.

	+	1 \$ .	
Acid	16	327	324
Base	57	67 <u>1</u>	$67\frac{3}{4}$
Water	27	0	0
Total	100	100	100

# Sp. 3. Fluate of Barytes.

THIS salt, as Bergman informs us, may be formed by pouring fluoric acid into nitrate or muriate of barytes. Fluate of barytes precipitates in the form of a white powder, which requires a considerable proportion of water to dissolve it.

## Sp. 9. Fluate of Alumina-and-Soda.

Chie suit is so

THIS curious compound has been found native in Greenland, and described by mineralogists under the name of *cryolite*. It has the appearance of a stone.

Its colour is greyish white; it has some transparency; when broken its fragments are cubical. It is softer than fluor spar, brittle, and of the specific gravity 2.950. Before the blow-pipe it melts. According to the analyses of Klaproth and Vauquelin it is composed of

† Gren's Handbuch, i. 533. This analysis is very erroneous. It is ascribed to Scheele; but I cannot find it in either of the dissertations on fluoric acid written by that illustrious chemist. It is given by Kirwan, without quoting Scheele.

Klaproth, Beitrage, iv. 365.

‡ By my analysis. Vol. II.

in alkalies, and forms

Rr

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## SALT3.

Book II. Division III.

6	100 *	ingen bij	100+
Alumina	24		21
Soda	36		32
Acid and water	40		47

## Sp. 10. Fluate of Silica.

FLUORIC ACID, when obtained by the usual process in glass vessels, contains always a portion of silica, and forms therefore in reality a superfluate of that earth. If this solution be allowed to remain for a considerable time in a vessel not completely shut, it deposites small brilliant, transparent, rhomboidal crystals. These Foureroy has ascertained to be fluate of silica. The acid may be separated by means of heat, and by concentrated acid. This salt is soluble in alkalies, and forms with them triple salts ‡. The silica which precipitates when fluoric acid prepared in glass vessels is absorbed by water, retains some of that acid even after it has been dried.

The fluate of strontian has not been examined.

SUCH is an imperfect detail of the properties of the fluates, a set of compounds which have hitherto attracted but little of the attention of chemists. The recent discovery of fluoric acid, however, as a constituent ofmany bodies in the mineral kingdom, where it was not suspected, will no doubt raise this neglected genus into

\* Klaproth's Beitrage, iii. 214. † Vauquelin, Hauy's Min. ii. 406.

‡ Fourcroy, iii. 111.

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## BORATES.

more repute, and induce some experimenter to favour the chemical world with a more complete detail. Richter indeed seems to have subjected the greater number of them to an analysis. The following Table exhibits the result of his experiments and calculations \*.

Fluates of Alumina		
Magnesia	. 100	144
Ammonia	. 100	157
Lime	. 160	186
Soda	.100	
Strontian	.100	311
Potash		
Barytes	. 100	

Constituents of the fluates.

Characters.

5 .0

Finite

III. Uses of the Fluates.

L Spritzin Bezatzz

THE only fluate hitherto applied to any use is the fluate of lime. In Derbyshire it is turned into boxes, candlesticks, and various trinkets: it is employed to facilitate the fusion of different kinds of ores. From it all the fluoric acid is procured, to what use soever that acid is to be applied.

Init salt, which was brut formed by Baton, is very

## GENUS III. BORATES.

from the experiments of Wenzel, the p

THOUGH some of these salts have been long known, and one of them has been in general use for many years, their nature is still but imperfectly understood, because

site said whitehouse be formed by saturation borag

\* I have not been able to procure a sight of Richter's very curious and important writings on Stechiometry, in which his observations on the fluates are to be found. The table in the text was calculated from a short table given by Fischer in Berthollet's Statique Chemique, i. 136. Chap. III.

Book II. Division III. they have been but superficially examined. Fourcroy is the only chemist, if we except Bergman, who has attempted a description of them. They may be distinguished by the following properties :

Characters.

1. Before the blow-pipe they melt into a glass.

2. When their concentrated solutions are boiled with sulphuric acid, and allowed to cool, brilliant scales of boracic acid are deposited.

3. They are not altered by combustible bodies.

4. With most metallic oxides they enter into fusion, and form globules of coloured glass.

I. SOLUBLE BORATES.

# Sp. 1. Borate of Potash.

THIS salt, which was first formed by Baron, is very little known. It may be prepared by calcining a mixture of boracic acid and nitre. The heat drives off the nitric acid, and leaves a white saline mass, which, when dissolved in water, yields crystals of borate of potash in four-sided prisms. It is capable of combining with an excess of base, and forming a sub-borate of potash. From the experiments of Wenzel, the proportion of its constituents seems to be \*.

Sp. 2. Borate of Soda.

THIS salt, which may be formed by saturating borax with boracic acid, has never been examined. Bergman

\* Verwandtschaft, p. 228-

#### BORATES.

informs us, that about half its weight of boracic acid is necessary to saturate borax\*. Its specific gravity is 1.351 +. It is soluble in 2.5 of water at the temperature of 147° ‡. From the experiments of Wenzel, the proportion of its constituents seems to be §

> Acid.....100 Base..... 44

## Sp. 3. Borax or Sub-borate of Soda.

This salt, the only one of the borates which has been accurately examined, is supposed to have been known to the ancients, and to be the substance denominated *chrysocolla* by Pliny. At any rate, it is mentioned by Geber as early as the ninth century under the name of *borax*. Its composition was first pointed out by Geoffroy in 1732, and Baron in 1748. Bergman was the first who demonstrated that it has an excess of base, and is therefore in the state of a sub-borate.

This salt is brought from the East Indies in an impure state under the name of *tinkal*, enveloped in a kind of fatty matter, which Vauquelin has ascertained to be a soap with soda for its base. When purified in Europe, it takes the name of *borax*. The purification is performed by the Dutch; but the process which they follow is not known. Valmont Bomare informs us that they extract 80 parts of pure borax from 100 parts of tinkal. The operations are conducted in leaden vessels, and consist chiefly in repeated solutions, filtrations, and

\* Bergman, iii. 325. According to Withering, twice its weight is necessary.-Bergman's Sciegraphia, p. 26. Eug. Trans.

\* Wenzel, Ibid. p. 309. § Verwandtschaft, p. 248.

History.

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<sup>+</sup> Hassenfratz, Ann. de Chim. XXVIII. 12.

Book II. Division III. crystallizations. Valmont Bomare suspects that they employ lime-water; and Fourcroy has shown that this might be useful in decomposing the soap in which crude borax is enveloped \*.

Properties.

Borax, thus purified, may be obtained crystallized in hexangular prisms, of which two sides are much broader than the remainder, and terminated by triangular pyramids. It is of a white colour. Its specific gravity is 1.740 +. It converts vegetable blues to green. Its taste is styptic and alkaline.

It is soluble, according to Wallerius, in 20 times its weight of water of the temperature of 60°, and six times its weight of boiling water. . brynecolla by Pline.

When exposed to the air it effloresces slowly and slightly.

When heated, it swells, loses about four-tenths of its weight, becomes ropy, and then assumes the form of a light porous, and very friable mass, known by the name of calcined borax; in a strong heat it melts into a transparent glass still soluble in water.

When two pieces of borax are struck together in the dark, a flash of light is emitted 1.

Composition.

This salt, according to Bergman, is composed of 39 acid theread by the Lorent

17 soda 44 water 100 ||

no and indestor

\* Fourcroy, iii. 330.

+ Kirwan. Wallerius makes it 1.720 (Chemistry, p. 266); Dr Watson, 1.757 (Essays, v. 67).

‡ Accum, Nicholson's Jour. ii. 28. || Bergman's notes on Scheffer.

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## Sp. 4. Borate of Ammonia.

This salt has been described by Wenzel. It forms permanent crystals, which have a considerable resemblance to borax. When heated the ammonia flies off, carrying with it a portion of the acid, but leaving a part of it in a state of purity. From the experiments of Wenzel, its constituents are \*

# 100 acid 34 base and water.

# Sp. 5. Borate of Strontian.

THIS salt has only been formed by Dr Høpe. It is a white powder, soluble in about 130 parts of boiling water. The solution turns the syrup of violets green  $\dagger$ . It is therefore in a state of a sub-borate.

> II. INSOLU-BLE BO-RATES.

## Sp. 6. Borate of Magnesia.

BERGMAN formed this salt by dissolving magnesia in boracic acid. The solution proceeded slowly; and on evaporation, the salt was precipitated in small irregular crystals. It is soluble in acetic acid. Alcohol decomposes it. It melts easily in the fire without being decomposed ‡. This salt has been found native in the mountain of Kalkberg near Luneburg in Germany. It was first analysed by Westrumb in 1788.

\* Verwandtschaft, p. 249. 2 Bergman, i. 386. + Hope, Edin. Trans. iv. 17.

Chap. III.

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Found naeive. It is in the form of transparent or opaque white crystals, consisting of cubes, having their edges and four of their angles truncated. It is so hard as to scratch glass, and to strike fire with steel. Its specific gravity is 2.566. When heated, it becomes electric; and, what is singular, the truncated angles are always positively electric, while the opposite entire ones are negative \*.

These crystals are insoluble in water, and not altered by exposure to the air. When heated, they decrepitate: in a red heat they lose their lustre, but do not sensibly diminish in weight. In a white heat they lose 0.005 of their weight. When exposed to the action of a very violent heat, they melt into a yellow-coloured glass.

According to Westrumb, they are composed of

73·5 acid 14·6 magnesia 11·9 lime

## 100.0

Hence the salt was considered as a triple compound of boracic acid, lime, and magnesia; but Vauquelin has shown, that the lime is foreign, and that the mineral is borate of magnesia  $\ddagger$ .

# Sp. 7, Borate of Lime.

Wolcz ei glan elmanns

THIS salt may be formed by mixing together limewater and the aqueous solution of boracic acid, or by boiling together lime and pure borax in water. In ei-

# Hauy, Ann, de Chim. ix. 59. | Nicholson, ii. 120, Second Series.

#### BORATES.

ther case, the borate of lime precipitates in the state of Chap. III. a white powder, tasteless, and difficultly soluble in water \*.

## Sp. 8. Borate of Barytes.

An insoluble white powder, which has scarcely been examined, formed by the same process as borate of lime.

## Sp. 9. Borate of Alumina.

THIS salt may be formed by mixing together the solutions of borate of soda and sulphate of alumina. It is said to be scarcely soluble in water, and not to crystallize.

When boracic acid and silica are exposed to a strong heat, they melt together into a transparent glass. This compound has received the name of *borate of silica* from Fourcroy.

The other borates are unknown.

OF THE BORATES.

THE only salt belonging to this genus that has been applied to any useful purpose, is borax. It is sometimes used in medicine as an astringent. It is used as a flux for metals, and enters into the composition of some of the coloured glass pastes made in imitation of gems; but its great use is to facilitate the soldering of the more precious metals. It is employed also as a flux by mineralogists in essaying the properties of minerals by the blow-pipe.

\* Bergman, iii. 363.

Book II. Division II.

## GENUS IV. PHOSPHATES.

THIS class of salts was first distinguished by Pott and Margraff. Several of the phosphates were afterwards examined by Haupt \*, Schlosser +, Rouelle ‡, Proust §, Westrumb and Scheele; but for the most complete account of them we are indebted to Fourcroy and Vauquelin. They may be distinguished by the following properties:

Characters.

- 1. When heated along with combustibles, they are not decomposed, nor is phosphorus obtained.

-2. Before the blow-pipe they are converted into a globule of glass, which in some cases is transparent, in others opaque.

3. Soluble in nitric acid without effervescence, and precipitated from that solution by lime-water.

4. Decomposed, at least partially, by sulphuric acid; and their acid, which is separated when mixed with charcoal and heated to redness, yields phosphorus.

5. After being strongly heated, they often phosphoresce.

The phosphates, like the sulphates, readily combine with an excess of acid, and form supersulphates.

The phosphates at present known amount to 12; two of which are triple salts. Some of these salts occur in different states, constituting varieties ||.

\* De Sale Mirabile Perlato, 1740.

1 Jour. de Medicine, 1776.

† De Sale Urinæ, 1760. § Jour. de Pbys. xvii. 148.

|| In the description of the phosphates given in most systematical works, they have been confounded with the *phosphites*. Fourcroy alone, guided by the experiments of Vauquelin, has observed the distinction

# Sp. 1. Phosphate of Potash.

OF this salt there are two varieties: The first, which is in reality a *superphosphate*, was first described by Margraff in 1740<sup>\*</sup>, and distinguished from the phosphate by Lavoisier in 1774. The second, which is a neutral salt, was also noticed by Margraff in 1746<sup>+</sup>, but its constituents remained unknown till they were lately ascertained by Darracq<sup>±</sup>.

Variety 1. Superphosphate. This salt may be prepared by dropping carbonate of potash into diluted phosphoric acid till all effervescence ceases, and then evaporating the solution. It crystallizes with great difficulty into striated prisms; assuming more readily the form of a jelly, and when the evaporation is carried farther, becoming dry altogether. Its specific gravity, when dry, is 2.8516 §. It is exceedingly soluble in water; and when dry readily attracts moisture from the atmosphere, and is converted into a viscid liquid. When heated, it first undergoes the watery fusion; then allows its water of crystallization to evaporate, and is reduced to dryness. In a high temperature it melts into a transparent glass, which deliquesces again when exposed to the air.

Variety 2. *Phosphate*. This salt may be formed by mixing together superphosphate of potash and pure pot-

throughout. Indeed there is strong reason to suspect, that the difference between these two genera of salts depends more upon other circumstances than upon the nature of the acid.

\* Opusc. i. 24. + Ibid. p. 162. † Ann. de Chim. xl. 179. § Hassenfratz, Ann. de Chim. xxviii. 12. 619

Chap. III. I. Soluble Phos-PHATES.

Book II. Division III. ash, and exposing them to a strong heat in a platinum crucible. A white coloured substance is obtained, which is the phosphate in question. Or we may boil any of the alkaline superphosphates in a solution of potash. A white powder falls, which is the salt wanted. By this last process it was procured by Margraf.

The phosphate of potash is tasteless and insoluble in cold water, but soluble in hot water; and it precipitates as the solution cools in a gritty powder. It is extremely fusible; melting before the blow-pipe into a transparent bead, which becomes opaque on cooling. It is soluble in natric, muriatic, and phosphoric acids: the solutions are thick, glutinous and adhesive. When sufficiently diluted, the alkalies occasion no precipitate in these solutions; but when they are concentrated, a precipitate appears.

According to the analysis of Saussure junior, its composition is as follows :

> acid 35 base 65

This salt has the property of combining, and of forming a triple insoluble compound with lime.

White Barked and W

# Sp. 2. Phosphate of Soda.

History.

THIS salt exists ready formed in urine, and was the first known of all the phosphates. It occupied a good deal of the attention of chemists; and the difficulty of analysing it gave occasion to various hypotheses con-

\* Sur la Vegete. p. 321.

cerning its nature. Hellot remarked it in urine ; and Chap. III. described it, in 1737, as a salt different from those that had usually been observed. Haupt described it in 1740 under the name of sal mirabile perlatum, or " wonderful perlated salt." It was called perlated from the grey, opaque, pearl-like colour which it assumed when melted by the blow-pipe. Margraf examined it in 1 745, and found it would not yield phosphorus when treated with charcoal as the other salts of urine did, but ascertained that it contained phosphoric acid. Rouelle the Younger analysed it in 1776; and concluded from his experiments that it was a compound of phosphoric acid and soda \*; but Mr Proust, being unable to obtain phosphorus from it, concluded that its acid was not the phosphoric, but another analogous to the boracic+. To this substance, which Mr Proust actually obtained, Bergman gave the name of perlated acid, and Morveau afterwards called it ouretic acid. But Mr Klaproth soon after analysed it, and proved that it consisted of soda supersaturated with phosphoric acid 1. Scheele soon after made the same discovery §. The acid of Mr Proust, then, is merely phosphate of soda combined with phosphoric acid, or superphosphate of soda.

Dr Pearson, who introduced it into medicine as a purgative, gave the following process for preparing it:

Dissolve in a long necked matrass 1400 grains of Preparacrystallized carbonate of soda in 2100 grains of water at the temperature of 150°. Add gradually 500 grains

tion

\* Jour. de Med. 1776, Juillet. t Crell's Annals, 1785, i. 238.

+ Jour. de Phys. 1781, i. 145. § Ibid. ii. 387.

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Book II. Division III. of phosphoric acid of the specific gravity 1.85. Boil the liquor for some minutes; and while it is boiling hot, filtrate it, and pour it into a shallow vessel. Let it remain in a cool place, and crystals will continue to form for several days. From the above quantities of materials he has obtained from 1450 to 1550 grains of crystals. Apothecaries usually prepare it from the superphosphate of lime, obtained from bones by means of sulphuric acid. An excess of carbonate of soda is added to separate the lime. The liquid is then filtered and evaporated slowly till it crystallizes.

Properties.

Its crystals are rhomboidal prisms, of which the acute angles are 60°, and the obtuse angles 120°, terminated by a three-sided pyramid. Its specific gravity is 1:333\*. Its taste is almost the same with that of common salt. It is soluble at the temperature of 60° in about four parts of water, and in two parts of boiling water. This solution crystallizes on cooling; but, in order to obtain the salt properly crystallized, the solution should contain a slight excess of alkali. When exposed to the air, this salt very soon effloresces on the surface. When heated, it undergoes the watery fusion. At a red heat it melts into a white enamel. Before the blow-pipe it melts into a transparent globule, which becomes opaque on cooling, and its surface acquires a polyhedral figure. personal all dyny sylingrifte

It is not altered by combustibles nor metals. With metallic oxides it enters into fusion, and forms a coloured globule of glass. Sulphuric, nitric, and muriatic acids, decompose it partially, and convert it into *super*-

\* Hassenfratz, Ann. de Chim. xxviii. 12.

phosphate of soda. In this state it is more soluble in Chap. III. water, and not so easily crystallized; but may be obtained by proper evaporation in the state of thin scales, not unlike boracic acid. It was this superphosphate which Proust obtained, and which he considered as a peculiar acid. passing into the -

The greater number of earths may be fused along with this salt, and converted into glass.

# Sp. 3. Phosphate of Ammonia.

THIS salt also exists in urine, and seems to have been first accurately distinguished by Rouelle. It was afterwards examined by Lavoisier in 1774, and still more lately by Vauquelin \*. It is usually prepared by saturating with ammonia the superphosphate of lime obtained from bones, and evaporating the solution to such a consistency, that when allowed to cool the phosphate of ammonia is obtained in crystals.

It crystallizes in four-sided prisms, terminated by Proporties. equal-sided pyramids. Its taste is cooling, salt, and ammoniacal. Its specific gravity is 1.8051 +. It is soluble in four parts of water at the temperature of 60°, and in rather a smaller proportion of boiling water. It is by spontaneous evaporation that it is obtained in the state of regular crystals. It is not altered by exposure to the air. When heated, it undergoes the watery fusion : it then dries ; but if the heat be continued, it swells up, loses its alkaline base, and the acid melts into a transparent glass. It is the only one of the earthy and alkaline phosphates which can be decom-

> \* Jour. de l'Ecole Polytechnique. Hassenfratz, Ann. de Chim. xxviii, 12.

Probarti

Book II. Division III. posed by heat : hence the reason that it yields phosphorus when distilled along with charcoal.

It is decomposed by the sulphuric, nitric, and muriatic acids, and by the fixed alkalies and alkaline earths. It is capable of combining with an additional dose of acid, and of passing into the state of a superphosphate.

## Sp. 4. Phosphate of Magnesia.

THIS salt was first formed by Bergman in 1775\*. It has lately been examined with much precision by the indefatigable Vauquelin +. It is usually prepared by dissolving carbonate of magnesia in phosphoric acid, and evaporating the solution gradually till the salt crystallizes; but it may be obtained in large regular crystals by a much easier process, first pointed out by Fourcroy. Mix together equal parts of the aqueous solutions of phosphate of soda and sulphate of magnesia. No apparent change takes place at first; but in a few hours large transparent crystals of phosphate of magnesia make their appearance in the solution.

Preparation.

Properties.

Its crystals are six-sided prisms, the sides of which are unequal. It has very little taste; however, it leaves a cooling and sweetish impression upon the tongue: Its specific gravity is 1.5489 1. It requires about 15 parts of cold water to dissolve it. It is more soluble in boiling water, but it crystallizes in part as the solution cools. When exposed to the air, it loses its water of crystallization, and falls down in powder. When heat-

\* Opusc. i. 390.

+ Jour. de l'Ecole Polytechniques t Hassenfratz, Ann. de Chim. xxviii. 12.

ed moderately, it is also reduced to a dry powder. In Chap. III. a high temperature, it melts into a transparent glass.

# Sp. 5. Phosphate of Soda-and-Ammonia.

THOUGH this salt, known to chemists by the names of microcosmic salt and fusible salt of urine, was extracted from urine, and examined much sooner than any of the other phosphates, it was long before philosophers were able to form precise notions concerning its nature, or even to obtain it in a state of purity. Margraf was the first who pointed out the method of procuring it pure, and who published a detailed description of its properties. He showed that it contained ammonia, and that it yielded phosphorus; but he did not succeed in discovering its whole constituents\*. Fourcroy was the first who gave a precise account of the proportion of its component parts +. According to him, it is composed 

be altered by exposu soda v24 soda vogzo vd beated, it fail a at bas, showing 19 ammonia, abwog of ellet temperature melle mater 25 water distilled along with characte phosphorus is obtained. Fourcrey has escertained (001 the phosphate of ammo-

The properties of this salt are nearly those of the phosphate of soda and phosphate of ammonia joined together. It answers better than the first of them as a flux ; because the heat soon drives off the ammonia, and leaves an excess of acid. Its specific gravity is 1.509 ‡. When exposed to the air, this salt effloresces, and gradually lo-

+ Ann. de Chim. vii. 183. \* Opusc. i. 123. † Hassenfratz, Ann. de Chim. xxviii. 12. Vol. II. Ss

Book II. Division III. ses its ammonia; a fact first observed by the Duke de Chaulnes. Margraf had observed that the ammonia is dissipated when the solution of it in water is evaporated.

## Sp. 6. Phosphate of Ammonia-and-Magnesia.

THIS salt was first discovered by Fourcroy, who found it in a calcalous concretion formed in the colon of a horse. Since this discovery, Fourcroy and Vauquelin have observed it also in human urine.

It might be prepared by mixing together solutions of the phosphates of ammonia and of magnesia in water; the triple salt immediately precipitates in the state of a white powder. When urine is allowed to remain a considerable time in close vessels, it often deposites this salt in regular crystals on the sides and bottom of the vessel. These crystals are small four-sided prisms, terminated by irregular four-sided pyramids. This salt is tasteless, scarcely soluble in water, and not liable to be altered by exposure to the air. When heated, it falls to powder, gives out its ammonia, and in a high temperature melts into a transparent globule. When distilled along with charcoal, phosphorus is obtained. Fourcroy has ascertained that the phosphate of ammonia-and-magnesia, obtained from the calcalous concretions of the horse, is composed of

33 phosphate of ammonia 33 phosphate of magnesia 33 water

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t Hassenfratz, Ave. 2 Per-

# Sp. 7. Phosphate of Lime.

OF this salt there are two varieties; the first neutral, in nitric and muriatic sold the other a supersalt.

Variety 1. Phosphate of Lime. This interesting salt, which constitutes the basis of bones, was pointed out by Scheele and Gahn in 1774: but for the first precise account of its properties we are indebted to Eckeberg\*, ime ; but the decon Fourcroy, and Vauquelin +.

As this salt constitutes the basis of bones, it is not Preparanecessary to prepare it artificially. It may be obtain- tion. ed in a state of purity by the following process: Calcine the bones to whiteness, reduce them to powder, and wash them repeatedly with water, to separate several soluble salts which are present. Dissolve the whole in muriatic acid, and precipitate by means of ammonia. The precipitate, when well washed and dried, is pure phosphate of lime.

Phosphate of lime, thus prepared, is always in the Properties. state of a white powder; but it is found native in regular crystals. In that state it is known by the name of apatite. The primitive form of its crystals is, according to Hauy, the regular six-sided prism; and the primitive form of its integrant particles is a three-sided prism, whose bases are equilateral triangles : But it very often assumes other forms. It is destitute of taste, insoluble in water, and not liable to be altered by exposure to the air. It may be exposed to a strong heat without undergoing any change ; but in a very violent

Crell's Annels, 1798, i. 323-

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& Jour de Pran

+ Mem. de l'Instit. ii. 274.

Ss 2

Book II: Division III. heat it becomes soft, and is converted into a white semitransparent enamel, or rather porcelain. According to the experiments of Saussure, a heat of 378° Wedgewood is necessary to produce this effect \*. It is soluble in nitric and muriatic acid without effervescence, and may be again precipitated from them unaltered by muriate of ammonia.

Sulphuric, nitric, muriatic, fluoric, and several vegetable acids, are capable of decomposing phosphate of lime; but the decomposition is only partial. Fourcroy and Vauquelin have ascertained, that these acids are only capable of abstracting 0:40 parts of the lime, while the remainder continues combined with the phosphoric acid, constituting a superphosphate of lime. Hence the reason that phosphoric acid is capable also of decomposing partially the combination of these acids with lime; it abstracts as much of the lime as is sufficient to convert it into superphosphate. The constituents of phosphate of lime, according to the most accurate analyses, are as follows : story a tal somit to standard

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the states		30.5	39	41	45	of apatite.
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- \* Jour. de Phys. xlv. 26. + Klaproth's Beitrage, iii. 20f.
- ‡ Eckeberg, rell's Annals, 1798, i 331.
- Richter, Statique Chemigue, 1. 136. 5 Fourcroy and Vauquelin.

These analyses do not differ much from each other, if Chap. III. we except the first, which doubtless gives the proportion of acid too small \*. The state of the s

Variety 2. Superphosphate of Lime. This variety was first distinguished as a peculiar compound in 1795 by Fourcroy and Vauquelin. It had indeed been often formed before, but chemists had neglected to examine it. It is this salt which always remains in the aqueous solution, when calcined bones are decomposed by means of sulphuric acid : and it may be formed artificially by dissolving phosphate of lime in phospharie acid, till the acid refuses to take up any more, and afterwards evaporating the solution till the salt crystallizes.

Its crystals are usually thin brilliant plates, resem- Properties. bling mother.of-pearl, which easily adhere together, and acquire a kind of gluey consistency. Its taste is strongly acid. Water dissolves it, and in a greater proportion when boiling hot than when cold : hence a saturated solution of it in boiling water crystallizes on cooling. It attracts a little moisture when exposed to the air. barytes, cr.

When heated, it readily undergoes the watery fnsion; then swells up and dries. In a high temperature it melts into a semitransparent glass, which is tasteless and insoluble, and is not altered by exposure to the air. When this salt is heated to redness along with charcoal, its excess of acid is decomposed, and converted into phosphorus, and phosphate of lime remains behind. It

\* Klaproth indeed elsewhere gives the constituents of this salt exactly as in the last column of the table in the text.

its compotent parts is u

42

Prepara, tion,

Book II. Division HI. is from this salt that phosphorus is usually obtained : but the process of Fourcroy, which consists in decomposing the superphosphate of lime by means of acetate of lead, and afterwards decomposing the phosphate of lead by means of charcoal, must yield a much greater proportion of phosphorus.

No acid hitherto tried is capable of decomposing this salt, except the oxalic, which abstracts its base completely, and precipitates with it in the form of oxalate of lime: but it is decomposed and reduced to the state of phosphate of lime by all the alkaline and earthy bases. It is composed, according to the analysis of Fourcroy and Vauquelin, of.....54 acid

## 46 lime

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Sp. 8. Phosphate of Barytes.

THIS salt has hitherto been described only by Mr Vauquelin \*.

It may be prepared either by saturating phosphoric acid with barytes or carbonate of barytes, or by mixing together an alkaline phosphate and nitrate or muriate of barytes. In either case the phosphate of barytes precipitates immediately in the form of a white powder.

Properties.

Preparation.

> This salt is tasteless, incrystallizable by art, insoluble in water, and not altered by exposure to the air. Its specific gravity is 1.2867 +. When strongly heated it melts into a grey-coloured enamel. The proportion of its component parts is unknown.

> > \* Jour. de l'Ecole Polytechnique.

+ Hassenfratz, Ann. de Chim. xxviii. 12.

When phosphoric acid is dropt into a solution of Chap. III. barytes water, a precipitate of phosphate of barytes immediately falls; but this precipitate is redissolved by adding an excess of acid \*. Hence it follows, that this salt is capable of combining with an additional dose of acid, and forming a superphosphate of barytes.

## Sp. 9. Phosphate of Strontian.

THIS salt was first formed by Dr Hope ; but it was more particularly described by Vauquelin in 1797 +.

Like the former salt it may be formed by dissolving carbonate of strontian in phosphoric acid, or by mixing together nitrate of strontian and phosphate of soda. A white precipitate immediately falls, which is the phosphate of strontian.

This salt is tasteless, insoluble in water, and not al- Properties. terable by exposure to the air. It is soluble in an excess of phosphoric acid; a property which distinguishes it from phosphate of barytes. Before the blow-pipe it fuses into a white enamel, and at the same time emits a phosphoric light. It is completely decomposed by sulphuric. acid, but by no other. According to Vauquelin, it is Composicomposed of .....41.24 acid

58.76 strontian

## 100.00

## Sp. 10. Phosphate of Alumina.

THIS salt has only been examined by Fourcroy. It may be formed by saturating phosphoric acid with alu-

> \* Fourcroy and Vauquelin, Mem. de l'Instit. ii. 61. + Jour. de Min. An. vi. p. 13.

## Book II. Division I I

mina. It is a tasteless powder, insoluble in water. Dissolved in phosphoric acid, it yields a gritty powder, and a gummy solution, which by heat is converted into a transparent glass.

# Sp. 11. Phosphate of Yttria.

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This salt has only been formed by Vauquelin. When the solution of phosphate of soda is mixed with the sulphate, nurate, or mutiate of yttria, phosphate of yttria precipitates in gelatinous flakes \*.

# Sp. 12. Phosphate of Glucina.

THIS salt has been examined only by Vauquelin. He obtained it by pouring phosphate of soda into the solution of glucina in sulphuric, nitric, or muriatic acid. The phosphate of glucina is precipitated in the state of a white powder. It does not crystallize. It is tasteless, insoluble in water, unless it contains an excess of acid, and not liable to be altered by exposure to the air. When heated strongly, it melts into a transparent glass  $\dagger$ .

Properties.

SUCH are the properties of the phosphates as far as we are acquainted with them at present. Hitherto no

# Ann. de Chim. XXXV. 1;8.

 $\dagger$  Phosphoric acid and silica, when mixed together and exposed to a strong heat, melt into a beautiful transparent glass, which is not decomposed either by the action of acids or of alkalies. Fourcroy has given this compound the name of phosphate of silica; but it is essentially different from salts, and ought therefore rather to be ranked in some other class of bodies.

complete analysis of their constituents has been published except by Richter. The following Table exhibits the result of his experiments and observations \*.

 Phosphate of
 Acid.
 Base.

 Alumina
 100
 53.6

 Magnesia
 100
 62.8

 Ammonia
 100
 68.6

 Lime
 100
 81

 Soda
 100
 81

 Strontian
 100
 135.7

 Potash
 100
 164

 Barytes
 100
 2271

III. USES OF THE PHOS-PHATES.

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Four only of the phosphates have been hitherto applied to any useful purpose.

1. Phosphate of soda.—This salt has been introduced into medicine as a purgative; and as its taste is not disagreeable, it has been much employed. It is usually taken in broth, which it is employed to season instead of common salt. It may be substituted for borax to promote the soldering of metals. Mineralogists employ it as a flux when they examine the action of heat on minerals by means of the blow-pipe.

2. Phosphate of ammonia.—This salt is much em-, ployed as a flux in experiments with the blow-pipe. It enters also as an ingredient in those coloured glasses called *pastes*, which are made in imitation of precious stones.

3. Phosphate of soda-and-ammonia.-This salt, like

\* The near recombinite between the photo-and photolice has in-

- to of stateball and the state

. \* Statique Chemique, i. 136. Seine Antonio

Chap. HL.

Book H. Division HI. the preceding, is used in experiments with the blowpipe, and answers remarkably well on account of the readiness with which it parts with its ammonia.

4. Phosphate of lime.—This salt is employed for making cupels: from it also almost the whole of the phosphorus employed by chemists is extracted. It is employed likewise as a medicine in rickets.

GENUS V. PHOSPHITES \*.

These salts have been lately examined for the first time, and their properties described, by Fourcroy and Vauquelin +. They may be distinguished by the following properties:

Characters.

1. When heated they emit a phosphorescent flame.

2. When distilled in a strong heat, they give out a little phosphorus, and are converted into phosphates.

3. Detonate when heated with nitrate or oxymuriate of potash, and are converted into phosphates.

4. Converted into phosphates by nitrate or oxymuriatic acid.

5. Fusible in a violent heat into glass.

The phosphites at present known amount to eight.

nerals by means

Stones

I. SOLUBLE PHOS-PHITES.

Sp. 1. Phosphite of Potash.

This salt is formed by dissolving carbonate of potash

\* The near resemblance between the *phosp!ates* and *phosphites* has induced me to place them next each other; though it was necessary to separate them in the table of the arrangement.

t Jour. de l' Ecole Polytechnique, I. iv. 655-

in phosphorous acid, and evaporating the solution slowly till it deposites crystals of phosphite of potash. It crystallizes in four-sided rectangular prisms, terminated by dihedral summits. Its taste is sharp and saline. It is soluble in three parts of cold water, and still more soluble in boiling water. It is not altered by exposure to the air. When heated it decrepitates, and then melts into a transparent globule, which becomes opaque on cooling. It does not phosphoresce so evidently as the other phosphites, perhaps because it contains an excess of potash, which saturates the phosphoric acid as it forms.

OTEL & DEC 20-

49.5 potash 11.0 water 100.0

# Sp 2. Phosphite of Soda.

THIS salt may be prepared exactly in the same way as phosphite of potash. Its crystals are irregular foursided prisms or elongated rhomboids. Sometimes it assumes the form of square plates, or of plumose crystals. Its taste is cooling and agreeable. It is soluble in two parts of cold water, and scarcely more soluble in boiling water. When exposed to the air it effloresces. Before the blow-pipe it emits a beautiful yellow flame, and melts into a globule, which becomes opaque on cooling.

It is composed of.....16.3 acid 23.7 soda 60.0 water

100.0

\$35

Chap. III.

Book II. Division III.

### Sp. 3. Phosphite of Ammonia.

THIS salt may be prepared by the same processes as the two last described phosphites. It crystallizes sometimes in long transparent needles, and sometimes in four-sided prisms terminated by four-sided pyramids. It has a very sharp saline taste. It is soluble in two parts of water at the temperature of 60°, and still more soluble in boiling water. When exposed to the air, it attracts moisture, and becomes slightly deliquescent. When distilled in a retort the ammonia is disengaged partly liquid and partly in the state of gas, holding phosphorus in solution, which becomes luminous when mixed with oxygen gas. Before the blow-pipe on charcoal, it boils and loses its water of crystallization; it becomes surrounded with a phosphorescent light, and bubbles of phosphureted hydrogen gas are emitted, which burn in the air with a lively flame, and form a fine coronet of phosphoric acid vapour. This gas is emitted also when the salt is heated in a small glass bulb, the tube belonging to which is plunged under mercury. This salt is composed of 26 acid to small bobie

assumes the forsinomma 12 points, one to humose crysteries. Its taste is cryixw 22 d again the second of a second with the second of the secon

### Sp. 3. Phosphite of Ammonia-and-Magnesia. has

THIS salt may be formed by mixing together the aqueous solutions of its two component parts. It is sparingly soluble in water, and may be obtained in crystals; but its properties have not been examined with precision.

#### PHOSPHITES.

### - Sp. 5. Phosphite of Alumina. Chap. III.

This salt may be prepared by saturating phosphorous acid with alumina, and then evaporating the solution to a proper consistence. It does not crystallize, but forms a glutinous mass, which dries gradually, and does not afterwards attract moisture from the air. Its taste is astringent. It is very soluble in water. When heated, it froths and gives out phosphorus, but it does not readily melt into a globule of glass.

> II. INSOLU-BLE PHOS-PHITES.

### Sp. 6. Phosphite of Magnesia.

THIS salt is best formed by mixing together aqueous solutions of phosphite of potash or soda and sulphate of magnesia; the phosphite of magnesia gradually precipitates in beautiful white flakes. It has no sensible taste. It is soluble in 400 parts of water at the temperature of 60°, and scarcely more soluble in boiling water. When its solution is evaporated slowly, a transparent pellicle forms on its surface, flakes are deposited, and towards the end of the process small tetrahedral crystals are precipitated. When exposed to the air, it effloresces. When heated, it phosphoresces and melts into a glass which becomes opaque on cooling.

20 magnesia 36 water

### 100

## the of bollow Sp. 7. Phosphite of Lime.

THIS salt may be formed by dissolving lime in phosphorous acid. When the saturation is complete, the salt

Book II. Division III. precipitates in the state of a white powder. It is tasteless and insoluble in water; but it dissolves in an excess of acid, and forms a superphosphite. This last salt may be obtained in prismatic crystals by evaporating the solution. This salt is not altered by exposure to the air. When heated it phosphoresces and emits a little phosphorus. In a violent heat it melts into a transparent globule. PLATE SAME SAME BUSE

It is composed of 34 acid

51 lime 15 water

#### 100

### Sp. 8. Phosphite of Barytes.

and the sector the

THIS salt may be formed by pouring phosphorous acid into barytes water, or this last water into a solution of phosphite of soda. In either case phosphite of barytes precipitates in the form of a white powder. It is tasteless, and but very sparingly soluble in water, unless there be an excess of acid. It is not altered by exposure to the air. Before the blow-pipe it melts, and is surrounded with a light so brilliant that the eye can scarcely bear it. The globule which it forms becomes opaque as it cools. It is composed or ...

It is composed of 41.7 acid

51.3 barytes 7.0 water

### 100.0

Hitherto none of these salts have been applied to any useful purpose. Into salt may by for

### GENUS VI. CARBONATES.

Though several of the carbonates were in the hands of chemists, and employed by them in the greater number of their experiments, their nature and composition were entirely unknown till Dr Black discovered it in 1756. Since that time they have been examined with great attention by almost every chemist of eminence; so that at present no family of salts is more accurately understood. The first treatise on the subject was published by Bergman in 1774 \*.

They may be distinguished by the following properties :

1. When sulphuric acid is poured upon them, they Characters. effervesce violently, emitting carbonic acid gas.

2. When heated strongly, the carbonic acid is driven off, and the base remains in a state of purity. Some carbonates require a very violent heat to be thus decomposed; but the operation is facilitated by mixing them with charcoal, which decomposes the carbonic acid altogether.

3. The alkaline carbonates tinge vegetable blues green, and have an alkaline taste.

4. The alkaline carbonates are soluble in water; the carbonates with bases of the alkaline earths are insoluble, but dissolve when an excess of acid is added.

Many of these salts exist native; but they may be all formed artificially by dissolving or diffusing the base in water, and making carbonic acid gas pass into the liquid till it be saturated. At present 11 species are

\* Opusco i. I.

\* Opuse L Lar

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Book II. known, several of which are capable of combining with an excess of acid.

I. SOLUBLE CARBO-NATE6.

Sp. 1. Carbonate of Potash.

THIS salt has been long known to chemists; and before its composition was ascertained by Black, it was characterized by a great variety of names, according to the manner of preparing it; such as *fixed nitre*, salt of *tartar*, vegetable alkali, &c. Its properties were first described with precision by Bergman in 1774\*. There are two varieties of it; the first neutral, the second containing an excess of alkali.

Preparation. Variety 1. Carbonate. This salt is formed by saturating potash with carbonic acid, which is best done by exposing a solution of potash for a considerable time to carbonic acid gas, or by causing the gas to pass through a solution of potash till it refuses to absorb any more. The potash of commerce is a compound of this salt and pure potash : By distilling it with solid carbonate of ammonia, it may be also converted into carbonate of potash †. When potash is saturated with carbonic acid, it always lets fall a quantity of silica. Mr Pelletier has proposed this saturation as the best method of purifying potash from the earth.

Properties.

It crystallizes, according to Bergman, in quadrangular prisms; the apexes of which are composed of two inverted triangles, converging like the roof of a house ‡. According to Pelletier they are tetrahedral rhomboidal

\* Opusc. i. 13.

+ Berthollet.

‡ Bergman, i. 13-

prisms, with dihedral summits. The complete crystal Chap. III. has eight faces, two hexagons, two rectangles, and four rhombs\*. It has an alkaline, but not a caustic taste, and still gives a green colour to vegetable blues. Its specific gravity is 2.012<sup>+</sup>. It is soluble at the common temperature in about four times its weight of water 1. Boiling water dissolves 5 ths of its weight §. Alcohol, even when hot, does not dissolve above Trachth part of it. Pelletier has observed, that when the crystallized salt is dissolved in boiling water, bubbles of carbonic acid gas are emitted. It is not altered by exposure to the air. Heat deprives it of its water and part of its acid, but does not decompose it completely.

The constituents of this salt, according to the most accurate analyses hitherto made, are as follows :

		T	**	<u>††</u>
Acid	20	26.5	43	43
Base	48	73.5	40	41
Water	32	1 - 200	17	16
Total	100	100	100	100

The coincidence between the experiments of Kirwan and Pelletier is very great, and induces us to confide

\* Ann. de Chim. XV. 29. + Hassenfratz, Ann. de Chim. xxviii. 12. || Bergman, Opusc. i. 14. † Bergman, i. 13. § Pelletier. Richter, Statique Chimique, i. 136. \*\* Kirwan, Nicholson's Quarto Jour. iii. 215.

+ Pelletier, Ann. de Chim. xv. 33-

Vol. II.

to Wedler

Book II. much more in their results than those of the other che-

Preparation.

Variety 2. Subcarbonate. The potash of commerce always occurs in this state; but its purity is destroyed. by the mixture of foreign substances. Pure subcarbonate of potash may be procured by heating neutral carbonate, prepared by the process above described, to redness, in a silver or platinum vessel. A portion of the carbonic acid is driven off. The subcarbonate thus formed has a stronger alkaline taste, and acts with more energy on animal and vegetable substances than the carbonate. When exposed to the air it soon deliquesces, and assumes the consistency of an oil. It does not absorb carbonic acid sensibly from the atmosphere; the excess of alkali cannot be removed by treating the salt with alcohol. Dr Wollaston has shown that this salt contains exactly one half of the acid which exists in carbonate of potash .\*.

Composition of potash of commerce. The potash of commerce is always in the state of a subsalt; but it contains likewise several foreign substances which render the proportion of alkali variable. Mr Kirwan has pointed out a very ingenious method of detecting the quantity of alkali in any specimen, by the property which it has of precipitating alumina from alum; and Vauquelin has published a still simpler method, namely, the quantity of nitric acid of a given density necessary to saturate a given weight of the salt. From his experiments, we learn that the following kinds of this salt known in commerce contain the following ingredients  $\dagger$ .

\* Wollaston, On superacid and subacid Salts, Phil. Trans. 1808.

CONTRACTOR .

+ Ann. de Chim. xl. 273.

#### \$42

Carbonic acid water. nsoluble re-30 Muriate of Sulphate potash. notash. Potash. sidue. Total. and Potash of Russia 772 5 56 254 65 1152 nerica 857 154 20 2 119 1152 American Pearl-ash 754 80 4 6 308 1152 Potash of Treves 720 165 44 24 199 1152 Dantzic 603 152 14 79 304 1152 -Vosges 444 148 510 34 304

### Sp. 2. Carbonate of Soda.

THIS salt has been also very long known. It is usually obtained by burning and lixiviating marine plants, or by decomposing common salt. In commerce it is called *barilla* or *soda*. In that state, however, it is never perfectly pure, containing always a mixture of earthy bodies, and usually common salt; but it may be purified by dissolving it in a small portion of water, filtrating the solution, and evaporating it at a low heat, skimming off the crystals of common salt as they form on its surface \*. Of this, like the preceding, there are two varieties; the first neutral, the second containing an excess of alkali.

\* See a detail of the different plants from which this substance is procured, and of the method of procuring them, in the Annales de Chimie, vol. alix, 267.

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Chap. III.

Book J . Division III. History. Variety 1. Carbonate. Though this salt occurs native in Africa in considerable quantities, it was not distinguished from the soda of commerce, which is a subcarbonate, possessing very different properties, till, in 1802, Klaproth published an account of it in the third volume of his works\*. It is found in the province of Sukena near Fezzan, and is called *trona* by the natives. It is crystallized in hard striated masses, not altered by exposure to the air, and of such hardness that the walls of Cassr, a fort now in ruins, are said to have been built of it.

This carbonate may be formed artificially by exposing the common subcarbonate of soda to an atmosphere of carbonic acid gas. In that situation it does not deposite crystals like subcarbonate of potash, but forms a solid shapeless mass, having some resemblance to the African carbonate.

When the carbonate of soda is exposed to a red heat, it loses its water of crystallization, and likewise a portion of its acid. Its constituents, as determined by the experiments of Klaproth, are as follows:

> Acid.....39 Base.....38 Water....23

Variety 2. Subcarbonate. What is usually called the carbonate of soda is merely this salt. It crystallizes in decahedrons, composed of two four-sided pyramids applied base to base, and having their apexes truncated  $\dagger$ .

\* Beitrage, iii. 83.

+ Bergman, i. 19-

It is often obtained also in large transparent flat rhomboidal prisms. Its taste is precisely the same with that of the carbonate of potash. Its specific gravity is 1.3591\*. It is soluble in two parts of cold water, and in rather less than its weight of boiling water. So that when dissolved in boiling water it crystallizes as the solution cools. When exposed to the air, it very soon effloresces and falls to powder. When heated, it undergoes the watery fusion; indeed the soda of commerce sometimes contains so much water of crystallization, that, when once melted, it remains permanently liquid. If the heat be continued, the water gradually evaporates, and the salt becomes dry. In a red heat it melts into a transparent liquid. A very violent heat drives off a part of its acid. This salt melts rather more easily than carbonate of potash, and for that reason it is preferred by glass manufacturers.

Its constituents, according to the analyses of it hitherto made, are as follows :

Examples.	+	1	ş	\$
Acid	16	16	14.42	40.14
Base	20	22	21.58	59.86
Water	64	62	64	
Total	100	100	100	100

\* Hassenfratz, Ann. de Chim. XXVIII. 12.

+ Bergman, Opuse, i. 18; and Fourcroy, Systems de Connoissances, iv. 56. Engl. Trans.

Tak Trent Light

‡ Klaproth, iii. 65. Engl. Trans.

§ Kirwan, Nicholson's Jour. iii. 215.

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Chap. III.

Book II. Division III. But either these analyses or that of the carbonate are inaccurate, or the salts examined were impure. For Dr Wollaston has shown, that when a pure carbonate of soda is exposed to a red heat it is converted into a subcarbonate, and loses exactly one half of its acid \*.

### Sp. 3. Carbonate of Ammonia.

Preparation. THIS salt has been also long known. It is often obtained by distilling animal substances; but for chemical purposes it is best to extract it from sal ammoniac by means of chalk. Two parts of chalk and one part of sal ammoniac, both as dry as possible, are mixed together and put into an earthen retort. On the application of a sufficient heat, carbonate of ammonia sublimes, and is obtained in the state of a white crystallized mass. This salt, like the other alkaline carbonates, is of two kinds, the *neutral* and *subcarbonate*.

Properties.

Variety 1. Carbonate. This salt may be obtained by exposing the common subcarbonate of ammonia to the air, or by causing a current of carbonic acid gas to pass through a solution of it in water. It crystallizes in sixsided prisms, usually small, has no smell, and less taste than the subcarbonate. According to the experiments of Schrader, it is composed of about

> 56 acid 19 base 25 water

#### 100 %.

Variety 2. Subcarbonate. This salt may also be ob-

# Phil. Trans. 1808.

+ Gehlen's Jour. ii. 583.

tained in crystals, but they are so small and so irregular, Chap. IIL. that it is difficult to ascertain their form. According to Bergman, they may be obtained in octahedrons, having, for the most part, their two opposite apexes truncated \*. The taste and smell of this salt, though much weaker, are the same with those of pure ammonia. Like all the alkaline carbonates, it converts vegetable blues to green, precisely as pure alkalies do. Its specific gravity is 0.966 +. It is soluble in rather less than twice its weight of cold water. Hot water dissolves its own weight of it. Boiling water cannot be employed, because at that heat the carbonate is volatilized. It is not altered by exposure to the air. When heated it evaporates very speedilv.

Mr Davy has shown that the component parts of this Composisalt vary exceedingly, according to the manner of preparing it. The lower the temperature at which it is formed the greater is the proportion of acid and water which it contains; and, on the other hand, the higher the temperature the greater is the proportion of alkali. Thus carbonate of ammonia, formed at the temperature of 300°, contained more than 50 per cent. of alkali, while carbonate formed at 60°, contained only 20 per cent. 1. Its constituents of course must be variously stated by chemists, according to the state in which they found it. The following table exhibits some of these results.

\* Bergman, i. 21. + Hassenfratz, Ann. de Chim. xxviii, 12. + Davy's Researches, p. 75.

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2

	‡	\$		9
Acid	45	48 to 50	50 t <b>o</b> 52	68.5
Base	43	_		31.5
Water	12		105	- AN
Total	100			100

Sp. 4. Carbonate of Ammonia-and-Magnesia.

THIS salt has been formed by Fourcroy by mixing together aqueous solutions of its two component parts; but it properties have not been examined.

II. INSOLU-BLE CAR-BONATES.

Prepara-

tion.

### Sp. 5. Carbonate of Magnesia.

THIS salt has been long known. Its composition was first discovered by Dr Black; afterwards its properties were investigated by Bergman and Butini, and more lately by Fourcroy \*. There are two varieties of it: the first neutral; the second containing an excess of base.

Variety 1. Subcarbonate. This salt is usually prepared by mixing together the solutions of sulphate of magnesia and carbonate of potash, and applying heat. The carbonate of magnesia precipitates in the state of a white powder. Such is the state in which it occurs in

- † Bergman, i. 21.
- § Schrader, Gehlen's Jour. ii. 583. When in a solid mass.
- || Ditto. When crystallized.
- ¶ Kirwan, Nicholson's Quarto Jour. iii. 215.
- \* Ann. de Chim. ii. 278.

commerce; but Fourcroy has shown that in that state it does not contain a maximum of acid. It is therefore only a subcarbonate; but it may be saturated with acid by diffusing it in water, and making carbonic acid gas pass through it till it be saturated and dissolved.

Variety 2. Carbonate. The carbonate, thus formed, yields by evaporation crystals which are transparent hexagonal prisms, terminated by a hexagonal plane: these are partly in groups and partly solitary: their length is about six lines, their breadth two \*. But it may be obtained in more regular crystals, by mixing together 125 parts of sulphate of magnesia and 136 parts of carbonate of soda, both dissolved in water, filtering the solution, and then setting it aside. In two or three days the carbonate of magnesia crystallizes.

This salt has little taste. Its specific gravity, when Properties. in powder, is only 0.2941 according to Hassenfratz t. It is soluble, when crystallized, in 48 parts of cold water ; but when in powder, it requires at least ten times as much; and what is very remarkable, it is more soluble in cold than in hot water impregnated with car-When exposed to the air, it effloresces, bonic acid 1. and falls into powder §. When heated, it decrepitates, falls into powder, and is decomposed.

The constituents of this salt are as follows :

\* Butini, sur le Magnesie. 1 Butini.

+ Ann. de Chim. xxviii. 12. § Fourcroy, Ann. de Chim. ii. 298.

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	*	+	1 #	ang si polotumor
Acid	50	30	36	a dees execute only s subcare of
Base	25	45	43	u a grientita y d u alguordi eacu
Water	25	25	21	Vatiety 2. G
Total	100	100	100	vielde by Green wina leaenstau

But the carbonate examined by the two last chemists does not seem to have been fully saturated with acid. The magnesia of commerce, according to Kirwan, is composed of ..... 34 acid

> 45 magnesia noduco to zruku 21 water moiselos orb menst

#### 1006

### Sp. G. Carbonate of lime.

THIS substance, under the names of marble, chalk, limestone, &c. exists in great abundance in nature, variously mixed with other bodies. It is perhaps the most important and most generally used of all the salts. unless we except muriate of soda. Its properties of course have been very completely investigated.

Propertica.

It is often found crystallized and perfectly transparent. The primitive form of its crystals is the rhomboidal prism with angles of  $101\frac{1}{2}^{\circ}$  and  $75\frac{1}{2}^{\circ}$ . Its integrant particles have the same form. But, besides the primitive, noless than 616 varieties of its crystals have been dis-

\* Fourcroy and Kirwan.

+ Bergman.

t Butini.

6 Nicholson's Jour. iii. 215.

covered and described by mineralogists. It has scarcely any taste. Its specific gravity is about 2.7. It is insoluble in pure water; but water saturated with carbonic acid dissolves  $r_{500}$  th part of it; from this solution it gradually precipitates, as the acid leaves it, in the form of a white powder \*. It suffers little or no alteration by being exposed to the air. When exposed to heat, it decrepitates and loses its water, and afterwards its acid separates as the heat is increased: But to separate the acid completely, a pretty strong heat is required.

Normal Dist	+	‡	\$
Acid	34	45	50
Base	55	55	50
Water	11	in it	S.P.S
Total	100	100	100

Its component parts are as follows :

Composition.

Some very interesting experiments on the fusibility of this salt were made by Sir James Hall. The result was, that when the carbonic acid is prevented from making its escape by strong compression, the salt melts at a red heat, and assumes an appearance which has some resemblance to granular limestone. A portion of the carbonic acid is usually dissipated. This portion is

\* Bergman, i. 26.

+ Bergman, Opusc. i. 23.

t Kirwan, Nicholson's Journal, iii. 215.

§ In this analysis the water is confounded with the acid. This water seems in crystallized pure carbonate to amount to three or four *per cent*. ; but I have not been able to ascertain its proportion, because the whole of it separates in combination with the carbonic acid. Book II. Division III.

sometimes very small, and very often it does not exceed 4 or 5 per cent. Bucholz has lately verified these experiments in a very unexpected manner. He put  $4\frac{1}{2}$  pounds of washed chalk (carbonate of lime with only 0.005 of foreign matter) into a crucible, pressed it strongly down, and exposed it covered to a strong heat in a furnace. The chalk, except a small portion on the surface, was converted into a foliated, hard, yellowish mass, having considerable transparency, which obviously had undergone a commencement of fusion. It was obviously in a similar state with Sir James Hall's carbonate of lime, and contained 42 per cent. of carbonic acid \*. Here the same effect was produced without compression. It must have depended no doubt upon the degree of heat to which the crucible was exposed.

### Sp. 7. Carbonate of Barytes.

THIS salt seems first to have been examined by Bergman. Withering first found it native in 1783. Hence it has received the name of *Witherite*. Since that time it has been examined by Kirwan, Klaproth, Hope, Pelletier, Fourcroy, and Vauquelin, and its properties described with great precision. It may be prepared artificially by exposing barytes water to the open air, or by passing carbonic acid gas into it. In either case the carbonate precipitates in the state of a white powder.

Properties.

It is found native crystallized. Its crystals have been observed to assume four different forms; double

# Gehlen's Jour. 2d Series, i. 271.

Structure St. all

six-sided and double four-sided pyramids, six-sided co- Chap. III. lumns terminated by a pyramid with the same number of faces, and small radiated crystals half an inch in length and very thin, appearing to be hexagonal prisms rounded towards the point. It has no sensible taste; yet it is poisonous. Its specific gravity, when native, is 4.331; when prepared artificially, it scarcely exceeds 3.763.

Cold water dissolves I part, and boiling water <sup>1</sup>/<sub>100</sub> part of this salt. Water saturated with carbonic acid dissolves  $\frac{1}{830}$  part ¶. It is not altered by exposure to the air. It is decomposed by the application of a very violent heat ||, either in a black lead crucible, or when formed into a paste with charcoal powder.

The constituents of this salt, according to the experiments of different chemists, are as follows :

	*	+	**	‡	\$
Acid	7	20	21.67	22	22
Base	65	80	78.33	62	78
Water	28		rib.a.	16	
Total	100		100.00	100	100

Composition.

#### Carbonate of Strontian. Sp. 8.

THIS salt was first pointed out as distinct from the History. last species by Crawford in 1790; but we are indebted

[	Fourcroy	Ann.	de Chim.	iv. 64.

- \* Bergman, Opusc. i. 22. + Withering.
- . \* \* Aiken, Nicholson's Jour. xxii. 303.

& Kirwan, Nicholson's Quarto Jour. iii. 215.

| Dr Hope.

‡ Pelletier.

Book II. Division III. for the first accurate account of it to Dr Hope. His experiments were afterwards confirmed by Klaproth, Pelletier, Fourcroy, and Vauquelin. It has been found native at Strontian in Argyleshire and at Leadhills in Scotland. It is usually in striated semitransparent masses, which have a greenish tinge.

Properties.

It has no taste. It requires 1536 parts of boiling water to dissolve it \*. Its specific gravity is about 3.66. It is not altered by exposure to the air. When strongly heated in a crucible, it loses part of its acid; and this decomposition is facilitated by making it into a paste with charcoal powder. According to Saussure, it melts into a transparent glass at the temperature of 226° Wedgewood †. When thrown in powder on burning coals, it produces red sparks.

Its component parts are as follows : and dilli lo enome

	‡	ş	
Acid	30-2	30	30.0
Base	61.2	· 62	69.5
Water	8.6	8	0.5
Total	100.0	100	100.0

Composition.

Sp. 9. Carbonate of Alumina.

THE greater number of chemists have agreed in admitting the existence of this salt. Bergman could not

- \* Hope, Trans. Edin. iv. 5. † Hope, Trans. Edin. iv. 8. \$ Pelletier, Ann. de Chim. xxi. 135-
- Klaproth, Beitrage, i. 270. and Kirwan, Nicholson's Jour. iii. 215.

form it artificially; but he allows its existence, because Chap. III. when alum is mixed with an alkaline carbonate, part of the alumina remains in solution till the carbonic acid be driven off\*. Saussure has shown lately, that water saturated with carbonic acid, is capable of dissolving alumina; but this combination is destroyed by simple exposure to the air. Carbonate of alumina, then, cannot exist in a dry state. What had been considered formerly as a dry carbonate is a triple compound of alumina, carbonic acid, and the alkali employed in precipitating the alumina t.

### Sp. 10. Carbonate of Yttria.

THIS salt may be formed by precipitating yttria from its solution in acids by means of an alkaline carbonate. It is a white, tasteless, insoluble powder, composed of

> 18 acid 55 yttria 27 water waiv a cavigolda'i gniwol to the most accurate analysi

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#### Carbonate of Glucina. Sp. 11.

This salt has been examined only by Vauquelin. It may be prepared by precipitating glucina from its solution in acids by an alkaline carbonate, and washing the precipitate sufficiently with pure water. It is in the state of a white soft powder, which has a greasy feel. It has no taste, and is exceedingly light. It is insolu-

\* Bergman, i. 32. 1 Klaproth's Beitrage, iii. 67. + Jour. de Phys. Ili. 28.

Book II. Division III. decomposed, and its acid driven off by the application of heat.

### Sp. 12. Carbonate of Zirconia.

This salt was formed by Vauquelin by precipitating zirconia from its solution in acids by alkaline carbonates. It is a tasteles white powder, composed of

> 44.5 acid and water 55.5 zirconia

#### 100.0

When heated the carbonic acid is driven off. This salt is soluble in the three alkaline carbonates, and seems to form with them triple salts.

DRUMIN OHHE

SUCH are the properties of the carbonates. The following Table gives a view of their constituents according to the most accurate analysis:

Water.         Acid.         Base.         Water.           Ammonia         50         100         33.9         44.6           Magnesia         2         100         50         50           Potash         25         100         95.3         37           Soda         50         100         97.4         59           Lime         0         100         122         50           Strontian         0         100         231         50	Carbonatesof	Solubility in 100	DOVE	112		
Magnesia         2         100         50         50           Potash         25         100         95·3         37           Soda         50         100         97·4         59           Lime         0         100         122           Strontian         0         100         231	Carbonatesor		Acid.	Base.	Water.	co of
Potash       25       100       95·3       37         Soda       50       100       97·4       59         Lime       0       100       122         Strontian       0       100       231	Ammonia	50	100	33.9	44.6	qual
Soda         50         100         97'4         59           Lime         0         100         122         122           Strontian         0         100         231         100	Magnesia	2	100	50	50	
Lime 0 100 122 Strontian 0 100 231	Potash	25	100	95.3	37.01	1.102
Strontian 0 100 231	Soda	50	100	97'4	59	1201
	Lime	0	100	122	sster wh	i tis
They are present if all allowing the your	Strontian	0	100	231	ų ghiwo	Ro.
Y ttria 0 100 305.5 150	Yttria	0	100	305.5	150	
Barytes 0 100 354*5	Bary:es	0	100	354*5	g ii ben	Sie

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Chap. III.

Table of the constituents of the carbos nates.

siz. W

They

All the carbonates are insoluble in alcohol; but the alkaline subcarbonates are partially soluble in that liquid.

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III. USES OF THE CARBO-NATES-

Charactein

FROM the peculiar nature of the acid which exists in these salts, the alkaline carbonates were long confounded with their bases. The alkaline character of these bases is by no means destroyed by the presence of the acid, and it is easily removed either by means of heat, or by the action of some other base. Hence the alkaline carbonates are applied to all the uses for which the pure alkalies are adapted. These are too numerous and well known to require a particular detail. The use of carbonate of lime as a manure, a paint, and a medicine, under the names of lime, whiting, crab's eyes, &c. is *Vol. II.* U n

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equally well known. None of the other carbonates have come into use, except the subcarbonate of magnesia, which is occasionally employed as a medicine.

### GENUS VII. SULPHATES.

SULPHURIC ACID is capable of combining with all the alkalies and earths except silica. The sulphates are almost all capable of assuming a crystallized form. Their taste, when they have any, is almost always bitter. They may be distinguished from other saline bodies by the following properties.

Characters.

8 -

1. They are insoluble in alcohol. When they are dissolved in water, alcohol precipitates them from that liquid, and it precipitates them crystallized.

2. Heat does not readily decompose them. But to this there are numerous exceptions. Most of the earthy sulphates are decomposed by a red heat either partially or totally; part of the acid escapes unaltered, and part, as has been shown by the experiments of Gay-Lussac\*, is decomposed into sulphurous acid and oxygen gas. In the alkaline supersulphates the excess of acid is separated in the same way, partly unaltered, partly in the state of sulphurous acid and oxygen gas.

3. When heated to redness along with charcoal, they are converted into sulphurets.

4. When barytic water, or a solution of any salt containing barytes, is dropt into a solution of any of the sulphates in water, a copious white precipitate immediately falls, which is insoluble in acetic acid.

\* Mam. d' Arcueil, 1. 213.

#### SULPHATES.

The genus of sulphates contains more species than any other, owing to the great tendency which the acid has to form triple salts. Many of the sulphates are capable of combining with an excess of acid, and of forming supersalts.

### Sp. 1. Sulphate of Potash.

OF this salt there are two varieties. The first is neutral, the second contains an excess of acid.

Variety 1. Sulphate. This salt may be formed by saturating diluted potash with sulphuric acid, and then evaporating the solution gently till crystals appear. It seems to have been known at a very early period by chemists, and a great variety of names were given to it, according to the manner of forming it, or the fancy of the operator. Some of these names were, specificum Names, purgans, nitrum fixum, arcanum duplicatum, panacea bolsatica, sal de duobus, sal polychrest glaseri, &c. but it was commonly known by the name of vitriolated tartar till the French chemists called it sulphate of potash when they formed their new nomenclature in 1787\*.

When the solution of sulphate of potash is sufficiently Properties. diluted, it affords by evaporation hexahedral pyramids, or short hexangular prisms, terminated by one or more hexangular pyramids. But these crystals vary much in their figure, according to the care with which they are prepared.

It has a very disagreeable bitter taste. Its specific

\* Bergman called it alkali vegetabile vitriolatum, and Morveau vitriol of potash.

I. SOLUBLE SUL-PHATES,

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Uu 2

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Composigion.

gravity according to Wallerius \* is 2'298; according to Hassenfratz, 2 4073 +; according to Watson, 2.636 7. At the temperature of 60° it dissolves in 16 times its weight of water; in a boiling heat it is soluble in five times its weight §. When it is boiled in water, that liquid dissolves 0.242 parts, or nearly 4th of its weight of it ||.

It suffers no alteration when exposed to the air. When placed upon burning coals, it decrepitates, but suffers no other alteration. In a red heat it melts, and loses  $1\frac{1}{4}$ per cent. of its weight. It is sometimes luminous in the 

Its component parts, according to the analyses bithereruporating the solution to published, are as follows: month more of a communication

51.0	**	<u>††</u>	55		a Here,	919
Acid	36.4	38.5	40	42.2	45.2	45.3
Base	63.6	61.5	52	50.1	54.8	54.7
Water		n diana A.	8	7.2	l ylaga	enes, com
Total	100.0	100	100	100	100	100

Variety 2. Supersulphate. This salt may be prepared by heating together a mixture of three parts of sulphate

\* Chemistry, p. 265.

\* Chemical Essays, v. 67.

Wenzei's Verwandtschoft, p. 310.

\*\* Thenard and Roard, Ann. de Chim. lix. 69 .-

§§ Bergman, i. 133.

tt This is the result of my analysis. potash gave 128 of sulphate of barytes. If this contains 33 per cent. of acid, it will indicate 42.2.

||| Kirwan, Nicholson's Jour. iii. 215.

+ Ann. de Chim. xxviii. 12.

§ Bergman, i. 135.

¶ Ann. de Chim. x. 40.

++ Richter.

100 Grains of fused sulphate of

19 Wenzel, p. 54.

#### SULPHATES.

of potash and one part of sulphuric acid. It was first distinguished from the first variety by Rouelle senior.

It usually crystallizes in long slender needles, but it may be obtained in six-sided prisms. Its taste is acrid, and it reddens vegetable blues. It is soluble in five parts of water at the temperature of  $60^{\circ*}$ . It is scarcely altered by exposure to the air. When heated it melts readily and assumes the appearance of oil, but it becomes as white as ever when allowed to cool. A very violent and long continued heat dissipates the excess of acid, and converts it into sulphate. Dr Wollaston has shown, that this salt contains just twice as much acid as the sulphate  $\ddagger$ .

But besides these two varieties, there are several others not yet particularly described. At least I have found the proportion of acid to vary considerably in different states of the salt.

### Sp. 2. Sulphate of Soda.

THIS salt was first discovered by Glauber, a German chemist, and for that reason was long known by the name of *Glauber's salt*. He himself called it sal mirabile. It may be prepared by saturating soda with sulphuric acid; but it is more usually obtained by decomposing common salt in order to procure muriatic acid. Like the sulphate of potash, it is capable of existing in two states. In the one it is neutral, in the other it has an excess of acid.

Variety 1. Sulphate. This is the state in which the

\* Link, Crell's Annals, 1796, i. 26.

+ On superacid and subacid salts. Phil. Trans. 1808.

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#### Properties.

Book II. Division III. Properties. salt usually occurs in commerce, being prepared in great quanties by the manufacturers of sal ammoniac. Its crystals are transparent, and when formed by slow evaporation, are six sided prisms, terminated by dihedral summits. The sides of the prisms are usually channelled, and the crystals are almost always exceedingly irregular. Its specific gravity, according to Wallerius, is 2.246 \*; Dr Watson, by a method not susceptible of much precision (on account of the ready solubility of this salt), found it 1.380 <sup>+</sup>.

Its taste at first has some resemblance to that of common salt, but soon becomes very disagreeably bitter. It is soluble in 2.86 times its weight of water at the temperature of 60°, and in 0.8 of boiling water  $\ddagger$ . When heated to redness, so as to drive off its water of crystallization, and then pounded in a mortar, it dissolves in 3.3 its weight of water at the temperature of 144° §. When exposed to the air, it loses great part of its water, and falls into a white powder ||, but it is not otherwise altered. It loses about 56 per cent. of its weight ¶.

When exposed to heat, it first undergoes the watery fusion\*\*, then its water is evaporated, it is reduced to a white powder, and in a red heat it melts. Mr Kirwan has observed, that part of the acid, as well as the water, is driven off by the application of a strong heat ++.

\* Wallerius' Chemia Physica, 266.

↑ Chemical Essays, y. 66.
§ Wenzel, p. 309.

isting of exercise

‡ Bergman, i. 133.

Substances which fall to powder in this manner are said to effloresce.
 Wenzel, p. 312.

\*\* When substances, on the application of heat, melt by means of the water they contain, they are said to undergo the watery fusion. *†† Irisb Transactions.* v.

#### SULPHATES.

Its constituents, according to the most accurate analyses hitherto made, are as follows :

10 10 01	*.	†	<b>‡</b>	1
Acid	23.52	27	55.7	56
Base	18.48	15	44.3	44
Water	58.00	58	a sector	l d cara
Total	100	100	100	100

These analyses differ but little from each other; that of Kirwan is probably the nearest precision.

Variety 2. Supersulphate. When the sulphate of soda is dissolved in sulphuric acid, if the solution be set aside, it deposites spontaneously large rhomboidal crystals which contain an excess of acid. They effloresce in the air, and lose their excess of acid when moderately heated. At the temperature of 66° they dissolve in twice their weight of water ||.

### Sp. 3. Sulphate of Ammonia.

THIS salt was discovered by Glauber, and called by him secret sal ammoniac. It was also called vitriolated ammoniac. It may be prepared by saturating ammonia with sulphuric acid, or by decomposing sal ammoniac by means of sulphuric acid.

Kirwan, Ibid. The two first analyses were made upon the crystals of the salt, the two last upon the salt supposed free from waters

|| Link, Crell's Annals, 1796. i. 27.

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<sup>\*</sup> Kirwan, Nicholson's Quarte Jour. iii. 215.

<sup>+</sup> Bergman, i. 133. ‡ Wenzel's Verwandtschaft, p. 56.

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Composi-

Its crystals are generally small six-sided prisms, whose planes are unequal, terminated by six-sided pyramids. It has a sharp bitter taste. It is soluble in twice its own weight of water at the temperature of 60°, and in its own weight of boiling water. Water of the temperature of 144° dissolves 0.78 of its weight of this salt\*. When exposed to the air, it slowly attracts moisture.

When heated, it first decrepitates, then melts, and in close vessels sublimes, but with some loss of its alkali<sup>+</sup>. In that state it might be called *supersulphate* of ammonia, as it contains an excess of acid, has an acid taste, and reddens vegetable blues. When heated nearly to redness, the greatest part of it is decomposed, some sulphurous acid comes over and some ammonia, a great quantity of azotic gas is disengaged, and in all probability water is formed  $\ddagger$ .

Its constituents have been determined as follows :

97	ġ.	H	1
Acid	54.60	58.75	59:8
Base	14:24	41.25	40.2
Water	31.10		
Total	100	100	100
L &	14 A 14	16 - 216 - C	1

Wenzel, p. 309.

f Kirwan's Min. ii. 31.

1:3

- Hatchett, Phil. Trans. Ixxxvi. 314.
- & Kirwan, Nicholson's Quarto Jour. iii. 215.
- Wenzel's Verwandtschaft, p. 58.
- S Richter, Statique Chemique, j. 136.

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These analyses differ very much from each other in the proportion of ammonia. The statement of Kirwan appears to be the most correct.

### Sp. 4. Sulphate of Magnesia.

THIS salt is held in solution in the springs at Epsom in England, and was procured from them by evaporation more than a century ago. Hence the term Epsom salt. by which it was long distinguished. Some account of it was given by Grew in 1675; and in 1723, Mr Brown published a description of the process employed in extracting it from the springs, and in purifying it\*. In Italy it is manufactured from shistose minerals, containing sulphur and magnesia. By roasting these minerals, and then moistening them and exposing them to the air, the salt effloresces on their surface. By solution in water, with the addition of a little lime to precipitate any metallic substance that may be in solution, and repeated crystallizations, the salt is obtained in a state of purity +.

It exists in considerable quantity in sea-water; and the uncrystallized residuum in the salt pans, after all the common salt has crystallized, consists partly of this salt dissolved in water. This residuum is usually called bittern, and sometimes in Scotland spirit of salt.

Sulphate of magnesia crystallizes in quadrangular . Properties, prisms, whose planes are equal, surmounted by quadrangular pyramids, or by dihedral summits. The primitive form of its crystals is, according to Hauy, a four-sided prism, whose bases are squares. The form of

- \* Phil. Trans. XXXII. 348.
- Ann. de Chim. 11viii. 80. See also Gehlen's Jour. iii. 549.

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Eook II. Division III. its integrant particles is a three-sided prism, whose bases are rectangular isosceles triangles §§. The crystals are doubly refrangent.

It has an intensely bitter taste. Its specific gravity is 1.66 \*. At the temperature of 60° it is soluble in its own weight of water, and in less than two-thirds of its weight of boiling water  $\ddagger$ . The volume of water is increased  $\frac{4}{76}$  ths by adding the salt  $\ddagger$ . When exposed to the air it effloresces, and is reduced to powder. When exposed to heat it undergoes the watery fusion; and by increasing the temperature its water is evaporated, but it cannot be decomposed by means of heat. Before the blow-pipe it melts with difficulty into an opaque vitreous globule  $\ddagger$ .

The following Table exhibits the result of the experiments of different chemists to determine the proportions of the constituents of this salt.

	ş	11	¶	**	<del>††</del>	ş
Acid	29.35	30.64	32	33	61.9	63.32
Base	17	16.86	19	19	38-1	36.68
Water	53.65	52.50	49	48	er og bør	downib n
Total	100	100	100	100	100	100

Composition.

§§ Traité de Mineralogie, ii. 322.

Kirwan, Nicholson's Quarto Jour. iii. 215. || Wenzel, p. 62.
 Mojon, Ann. de Chim. xlviii. 81. \*\* Bergman, i. #35.

11 Richter, Statique Chemique, 1. \$36.

#### SULPHATES.

These analyses do not differ much from each other; probably a mean of the whole would come pretty near the accurate result.

### Sp. 5. Sulphate of Potash-and-Ammonia.

THIS salt, which was first described by Link, may be formed by saturating the supersulphate of potash with ammonia. The crystals are brilliant plates, having a bitter taste, and not altered by exposure to the air. They are composed of

> 60 sulphate of potash 40 sulphate of ammonia

100\*

### Sp. 6. Sulphate of Potash-and-Magnesia.

THIS salt, as well as the last, was first described by Link. He formed it by saturating supersulphate of potash with magnesia. Berthollet formed the same salt by mixing together equal solutions of sulphate of potash and muriate of magnesia, and evaporating the mixture. Crystals of sulphate of potash, with a little muriate of magnesia, are first obtained, and then the triple salt in rhomboidal crystals, which are not altered by exposure to the air. Their solubility is nearly the same as that of sulphate of potash  $\dagger$ .

The taste of this salt is bitter. It is composed of

3 parts sulphate of potash 4 parts sulphate of magnesia

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\* Link, Crell's Annals, 1796. i. 29. Link, Crell's Annals, 1796, i. 30. + Mem. de l' Instit. iii. 218.

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### Sp. 7. Sulphate of Soda-and-Ammonia.

THIS salt was first described by Link, who formed it by saturating supersulphate of soda with ammonia. Seguin formed it by mixing together the solutions of sulphate of soda and sulphate of ammonia, and evaporating the mixture. The triple salt is obtained in crystals. These crystals are regular, and are not altered by exposure to the air. Their taste is pungent and bitter. When heated they decrepitate and swell, ammonia is first disengaged, and supersulphate of ammonia and sulphate of soda remain. Soda decomposes it by driving off the ammonia \*.

According to Link it is composed of

5 parts sulphate of soda 9 parts sulphate of ammonia

### 14+

### Sp. 8. Sulphate of Soda-and-Magnesia.

LINK obtained this salt by saturating supersulphate of soda with magnesia, and evaporating the solution. The crystals are prismatic, large, have a bitter taste, and effloresce in the air. It is composed of

5 parts sulphate of soda

6 parts sulphate of magnesia

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# Jour. de Min. An. 10. p. 80. ‡ Link, Ibid. + Crell's Annals, 1796, i. 30.

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#### SULPHATES.

### Sp. 9. Sulphate of Magnesia-and-Ammonia.

This salt was pointed out by Bergman; but Fourcroy was the first chemist who examined its properties §. It may be prepared by mixing together saturated solutions of sulphate of ammonia and of magnesia. Crystals almost immediately precipitate, which consist of the two salts combined together. Or it may be prepared by pouring ammonia into a solution of sulphate of magnesia. Part only of the magnesia is precipitated. This is to be removed by filtration; and on evaporating the solution, the compound salt is obtained in crystals.

This salt crystallizes in octahedrons. Its taste is acrid and bitter. Its specific gravity is 1.696 \*. It is less soluble in water than either of its component parts. When heated it undergoes the watery fusion; and if the heat be increased, it is decomposed. It is not altered by exposure to the air.

It is composed, according to the analysis of Fourcroy, of

Composi-

68 sulphate of magnesia 32 sulphate of ammonia

100

### Sp. 10. Sulphate of Alumina.

THIS salt may be formed by dissolving alumina in sulphuric acid, evaporating the solution to dryness, dissolving it again in water, and evaporating it till it crystallizes. Little attention has hitherto been paid to this salt, which was never properly distinguished from *alum* 

§ Ann. de Chim. iv. 21.

# Hassenfratz, Ibid. xxviii. 121.

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Properties.

till two memoirs, one by Vauquelin and another by Chaptal, on the nature of alum, made their appearance in the 22d Volume of the *Annales de Chimie*.

It crystallizes in thin plates, soft and pliant, and of a pearly lustre. Its taste is astringent. It is very soluble in water, and does not crystallize without difficulty. When heated it loses its water of crystallization, and falls to powder. A strong heat decomposes it completely by volatilizing the acid. It is not altered by exposure to the air.

# Sp. 11. Alum.

Varieties.

OF this salt there are no less than four varieties, all of which are triple salts; two neutral, and two in the state of supersalts. These varieties may be distinguished by the following names:

1. Sulphate of alumina-and-potash.

2. Sulphate of alumina-and-ammonia.

3. Supersulphate of alumina-and-potash.

4. Supersulphate of alumina-and-ammonia.

The two last of these varieties are usually confounded together under the name of *alum*: the two first have been called *alum saturated with its earths*, and sometimes *aluminated alum*. It will be proper to consider the two last varieties first, because they have been longest known, and are the most important.

Variety 1. The supersulphates. The growther of the Greeks, and the alumen of the Romans, was a native substance, which appears to have been nearly related to green vitriol or sulphate of iron; and which consequently was very different from what we at present denominate alum. From the researches of Professor Beckman, it appears that we owe the discovery of alum

to the Asiatics; but at what period, or by what means, the discovery was made, is altogether unknown. It continued to be imported from the east till the 15th century, when a number of alum works were established in Italy. In the 16th century it was manufactured in Germany and Spain; and during Queen Elizabeth's reign an alum work was established in England by Thomas Chalomer. The alum of commerce is usually obtained from native mixtures of pyrites and clay, or sulphuric acid and clay.

Bergman has published a very complete dissertation on the process usually followed \*. The earth from which it is procured is usually called *aluminous schistus*, because it is slaty. Its colour is blackish, because it contains some bitumen. In most cases it is necessary to burn it before it can be employed; this is done by means of a slow smothered fire. Sometimes long exposure to the weather is sufficient to produce an efflorescence of alum on the surface. It is then lixiviated, and the water concentrated by evaporation, and mixed with putrid urine, or muriate of potash; crystals of alum and of sulphate of iron usually form together.

The composition of alum has been but lately understood with accuracy. It has been long known, indeed, that one of its ingredients is sulphuric acid +; and the experiments of Pott and Margraf proved incontestibly that alumina is another ingredient. But sulphuric acid and alumina are incapable of forming alum. Manufac-

\* Opusc. i. 279.

+ Some chemists have thought proper to call the sulphuric acid, obtained by distilling alum, spirit of alum. 671

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Book II. Division III. turers knew that the addition of a quantity of potash or of ammonia, or of some substance containing these alkalies, is almost always necessary; and it was proved, that in every case in which such additions are unnecessary, the earth from which the alum is obtained contains already a quantity of potash. Various conjectures were made about the part which potash acts in this case; but Vauquelin \* and Chaptal + appear to have been the first chemists that ascertained by decisive experiments that alum is a triple salt, composed of sulphuric acid, alumina, and potash or ammonia, united together.

Properties.

Alum crystallizes in regular octahedrons, consisting of two four-sided pyramids applied base to base. The sides are equilateral triangles. The form of its integrant particles, according to Hauy, is the regular tetrahedron. Its taste is sweetish and very astringent. It always reddens vegetable blues. Its specific gravity is 1.7109 1. At the temperature of 60° it is soluble in from 15 to 20 parts of water, and in  $\frac{3}{4}$  ths of its weight of boiling water. When exposed to the air it effloresces slightly. When exposed to a gentle heat it undergoes the watery fusion. A strong heat causes it to swell and foam, and to lose about 44 per cent. of its weight, consisting chiefly of water of crystallization §. What remains is called *calcined* or *burnt alum*, and is sometimes used as a corrosive. By a violent heat, the greater part of the acid may be driven off. In that case, as was first observed by Gay-Lussac, a portion of the

\* Ann. de Chim. xxii. 258.

+ Ibid. 280.

t Hassenfratz, Ann. de Chim. xxviii. 12. Wallerius found it 17.9 (Chemistry, p. 266); and Dr Watson, 1.757 Essays, v. 67); Fahrenheit, 1738. (Phil. Trans. liii. 114.) § Bergman, i. 287.

acid is decomposed into sulphurous acid and oxygen gas.

Though the properties of alum are in all cases pretty nearly the same, it has been demonstrated by Vauquelin that three varieties of it occur in commerce. The first is *supersulphate of alumina-and-potash*; the second, *supersulphate of alumina-and-ammonia*; the third is a mixture or combination of these two, and contains both potash and ammonia. It is the most common of all; doubtless, because the alum makers use both urine and muriate of potash to crystallize their alum. Vauquelin, Thenard, and Roard have lately analysed a number of specimens of alum manufactured in different countries. The result was that they all contain very nearly the same proportion of ingredients. The mean of all their trials was as follows:

	*	+
Acid	30.52	26.04
Alumina	10.20	12.53
Potash	10.40	10.02
Water	48.58	51.41
Total	100.00	100:00

## From the late analyses and experiments of Thenard

\* Vauquelin, Ann. de Chim. l. 167. Small quantities of ammonia also occurred in several,

+ Thenard and Roard, Ann. de Chim. lix. 72. The acid was estimated by means of sulphate of barytes, which they considered as containing only 26 per cent. of sulphuric acid; whereas it contains 33 per cent.; of course the proportion of that acid in the table is too small.

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and Roard, it appears that alum usually contains a little sulphate of iron. Its good qualities as a mordant in dyeing, depend upon the proportion of that salt present. The freer it is from it the better. The purest alum examined contained about  $\frac{1}{2000}$ th part of its weight of sulphate of iron, the impurest about  $\frac{1}{2000}$ . When freed from sulphate of iron every species of alum tried acts exactly in the same manner as a mordant \*.

Cubic alum.

When an unusual quantity of potash is added to alum liquor, the salt loses its usual form and crystallizes in cubes. This constitutes a *fourth* variety of alum, usually distinguished by the name of *cubic alum*. It contains an excess of alkali.

Fifth variety.

Neutral compounds.

Properties.

When the potash is still further increased, Chaptal has observed that the salt loses the property of crystallizing altogether, and falls down in flakes. This constitutes a *fifth* variety of alum, consisting of sulphate of potash combined with a small proportion of alumina.

Variety 2. The sulphates. All the varieties of alum are capable of combining with an additional dose of alumina, and forming perfectly neutral compounds; all possessed of nearly the same properties, and therefore confounded together as one salt.

It may be prepared by boiling a solution of alum with pure alumina; the compound, as it forms, gradually precipitates in the form of a white powder. It was formerly denominated *alum saturated with its earth*. This saft does not crystallize, but has always the torm of a tasteless powder. It is insoluble in water, and not.

\* Ann. de Chim. lix. 58.

altered by exposure to the air. Heat has no effect upon it unless it be very violent; and in that case part of the acid is disengaged. Sulphuric acid converts it into alum. It is less easily decomposed by other bodies than alum. Several of the acids dissolve slowly its last dose of alumina, and convert it into alum. This salt has not hitherto been applied to any use. Alum is capable also, as Chaptal informs us, of combining with several other bases, and of forming many triple salts, which have never yet been examined with attention \*.

If three parts of alum and one of flour or sugar be Homberg's melted together in an iron ladle, and the mixture dried till it becomes blackish and ceases to swell: if it be then pounded small, put into a glass phial, and placed in a sand-bath till a blue flame issues from the mouth of the phial, and after burning for a minute or two be allowed to cool +, a substance is obtained known by the name of Homberg's pyrophorus, which has the property of catching fire whenever it is exposed to the open air, especially if the air be moist.

This substance was accidentally discovered by Homberg about the beginning of the 18th century, while he was engaged in his experiments on the human fæces. He had distilled a mixture of human fæces and alum till he could obtain nothing more from it by means of heat; and four or five days after, while he was taking the residuum out of the retort, he was surprised to see it take fire spontaneously. Soon after, Lemery the Younger discovered that honey, sugar, flour, or almost any

Ann. de Chim. xxii. 293. / + Care must be taken not to keep it too long exposed to the heat. Xx2

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Book II. Division III. animal or vegetable matter, could be substituted for human fæces; and afterwards Mr Lejoy de Suvigny showed that several other salts containing sulphuric acid may be substituted for alum \*. Scheele proved that alum deprived of potash is incapable of forming pyrophorus, and that sulphate of potash may be substituted for alum †. And Mr Proust has shown that a number of neutral salts, composed of vegetable acids and earths, when distilled by a strong fire in a retort, leaves a residuum which takes fire spontaneously on exposure to the air.

These facts have thrown a great deal of light on the nature of Homberg's pyrophorus, and enabled us in some measure to account for its spontaneous inflammation. It has been ascertained, that part of the sulphuric acid is decomposed during the formation of the pyrophorus, and of course a part of the alkaline base becomes uncombined with acid ; and the charcoal, which } gives it its black colour, is evidently divided into very minute particles. It has been ascertained, that during the combustion of the pyrophorus a quantity of oxygen is absorbed. The inflammation is probably occasioned by the charcoal; the sulphuret of potash also acts an essential part. Perhaps it produces a sudden increase of temperature by the absorption and solidification of water from the atmosphere.

- \* See Macquer's Dictionary.
- + Scheele on Fire and on Pyropborus.

# Sp. 12. Sulphate of Yttria.

THIS salt was first formed by Gadolin, and afterwards it was examined with more precision by Eckeberg \*, Vauquelin +, and Klaproth t.

Sulphuric acid dissolves yttria readily, and some caloric is evolved during the process. As the solution goes on, the sulphate crystallizes in small brilliant grains.

These crystals are irregular, but most frequently, Properties. according to Eckeberg, they have the form of flat sixsided prisms terminated by four-sided summits. These crystals are not altered by exposure to the air. Their taste is astringent and sweetish, though not so much so as sulphate of glucina. Their colour is a light amethyst red; their specific gravity 2.791. They require at least 30 parts of water at the temperature of 60° to dissolve them. At a red heat they are partly decomposed.

Oxalic acid, prussiate of potash, and the infusion of nutgalls, occasion a precipitate in the aqueous solution of this salt. It is decomposed by phosphate of soda.

Sulphate of glucina is readily distinguished from this salt by its being colourless, lighter, and more soluble in water.

## Sp. 13. Sulphate af Glucina.

THIS salt was first examined by Vauquelin, the discoverer of its base.

\* Crell's Annals, 1799, ii, 68. † Ann. de Chim. XXXVI. 256 \$ Beitrage, iii. 67.

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Book I'. Division III. It is prepared by saturating sulphuric acid with glucina. The acid dissolves the earth readily, and the solution by evaporation yields small needle-form crystals, the figure of which has not been ascertained.

Properties.

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It has a very sweet and somewhat astringent taste, It is very soluble in water; the solution readily assumes the consistence of a syrup, but is brought with difficulty to crystallize. When heated it undergoes the watery fusion, loses its water of crystallization, and falls to powder. At a red heat it is decomposed completely, the acid is driven off, and the earth remains in a state of purity. The infusion of nutgalls, when dropped into the solution of this salt, occasions a yellowish white precipitate.

# Sp. 14. Sulphate of Zirconia.

THIS salt was first formed by Klaproth, but Vauquelin has described it with more precision. It is prepared by dissolving zirconia in sulphuric acid, and evaporating the solution to dryness.

Properties.

It is usually in the form of a white powder. It may, however, be obtained in small needle-form crystals. It has no taste, and is insoluble in water. It is not altered by exposure to the air. It is very easily decomposed by heat: The acid readily flies off, and leaves the earth in a state of purity. This decomposition may be accomplished even by boiling in water; the earth precipitates, and the acid remains in solution. Klaproth informs us, that with excess of acid sulphate of zirconia forms transparent stelliform crystals, soluble in water, and having an astringent taste \*.

\* Jour. de Phys. xxxvi. 187.

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# Sp. 15. Sulphate of Lime.

OF this salt there are two varieties. The first contains water, and is called common sulphate : The second, which is destitute of water, is called anhydrous sulphate.

Variety 1. Common sulphate. This salt was well known to the ancients under the name of gypsum; but the composition of gypsum was not known till Margraf and Macquer analysed it, and proved it to be a compound of sulphuric acid and lime. The salt formed by the artificial union of these two bodies was formerly called selenite, probably from its whiteness.

The properties of this salt were first examined with Properties. precision by Bergman. It is found abundantly in different parts of the world, so that it is seldom formed artificially. When pure, it is frequently crystallized. The primitive form of its crystals is, according to Hauy, a right angular prism with rhomboidal bases, whose angles are 113° and 67°. Its integrant particles have the same form ; but it is more usually found crystallized in octahedrons, in six-sided prisms, with four-sided summits, or lenticular. These crystals are often exceedingly transparent.

It has a slightly nauseous taste, scarcely perceptible, except by drinking a glass of water impregnated with it \*. It is soluble in 460 parts of water at the temperature of 60° +, and in 450 of boiling water. Mr Paul has observed, that if this solution be saturated by pres-

\* Macquer.

+ Bucholz, Gehlen's Jour. v. 165.

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sure with hydrogen gas, the sulphate in about six months is converted into a sulphuret ‡‡. The salt is not affected by exposure to the air. It is soluble in sulphuric acid.

When heated, it loses its water of crystallization, decrepitates, and falls into a soft white powder. This powder, when its water has been driven off by the application of a red heat, absorbs water very rapidly, and solidifies it; at the same time a slight increase of temperature takes place: so that if it be formed into a paste with water, it dries in a few minutes. In this state it is called *plaster of Paris*, and is much employed for forming casts, &c. in consequence of this property.

Sulphate of lime, when exposed to a violent heat, melts; before the blow-pipe it gives an opaque vitreous globule. The temperature necessary to produce this effect is, according to Saussure, 51° of Wedgewood §§.

The following Table exhibits the result of the different experiments hitherto made to ascertain the proportion of the constituents of this salt.

. [		*	+	‡	ş	*		**		++
	Acid	43	43	46	55.75	56.58	57	57.57	59	59.84
	Base	33	57	32	44.25	43.42	43	42.43	41	40.16
	Water	24		22		-		. 0	1000	(abril
	Total	100	100	100	100	100	100	100	100	100

\$\$ Phil. Mag. xv. 63.

- \* Bucholz, Gehlen's Jour. v. 162.
- Bergman, i. 135.

By my own analysis.

† Chenevix, Pbil. Mag. xi. 15. § Richter, Gehlen's Jour. v. 154. \*\* Klaproth, Ibid. ii. 359.

§§ Jour. de Phys. xlv. 16.

J Kirwan, Nicholson's Quarto Jour. iii. 215.

tt Wenzel.

These numbers, except the analysis of Chenevix, do not differ much from each other. The analysis of Bucholz seems most correct. It scarcely differs from the result of my experiments.

Variety 2. Anhydrous Sulphate. This variety is found native in different parts of the earth; Sweden, Tyrol, Berne, &c. It seems to have been first pointed out by Hauy. A specimen of it was described with much precision by Fleuriau in the Journal de Phisique for 1798; and analysed by Vauquelin, who first ascertained its composition. It has since been described with more precision by Bournon †, and a purer specimen of it analysed by Chenevix ‡, and more lately by Klaproth §.

It is usually crystallized. The primitive form of its crystals is a rectangular prism, having two of its faces broader than the other two. It has considerable lustre, and the broad faces have the appearance of pearl. Its specific gravity is about 2.950. Its hardness is considerable, being not inferior to that of calcareous spar. It usually phosphoresces when heated. It is transparent, insoluble in water, and in its other properties agrees with common sulphate.

In the proportions of its constituent parts it coincides exactly with common sulphate, excepting in the absence of water.

# Sp. 16. Sulphate of Barytes.

THIS salt is found abundantly in different parts of the earth, and was formerly denominated *ponderous spar*.

+ Jour. de Min. An. x. ii. 345. \$ Gehlen's Jour. ii, 355. \$ Jour. de Min. An. x. ii. 345. \$ Gehlen's Jour. ii. 355. 681

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Anhydrous Sulphate, Book II. Division III. from its great weight. Its composition was first ascertained by Gahn.

Properties.

Hauy has shown that the form of its integrant particles is a right-angled prism, whose bases are rhombs with angles of  $101\frac{1}{2}^{0}$  and  $78\frac{1}{2}^{0}$ . The primitive form of its crystals is the same; but it occurs native in a variety of other forms. It cannot be crystallized by art. This salt is insoluble in water, or at least only soluble in 43000 times its weight of water at the temperature of the atmosphere \*. Sulphuric acid dissolves it when concentrated and boiling, but it is precipitated by the addition of water  $\ddagger$ .

When suddenly heated, it breaks in pieces and flies about with a crackling noise. This phenomenon, which is called *decrepitation*, is occasioned by the sudden conversion of the water which it contains into steam. When heated very violently it melts, and before the blow-pipe is converted into a white opaque globule. According to Saussure, a heat equal to 35° Wedgewood is required to fuse it ‡. When formed into a thin cake with flour and water, and heated to redness, it phosphoresces in the dark. This was first observed in a variety of this substance known by the name of Bologna stone. Lemery informs us, that the property was discovered by an Italian shoemaker named Vincenzo Casciarolo.

\* Kirwan's Min. i. 136.

† Thus it forms a kind of supersulphate, capable of crystallizing, as Withering first observed. Mr Hume has also mentioned it in *Pbil. Mag.* Xiv. 357 The fact was well known to chemists. This solution, however, is but very imperfectly entitled to the name of supersulphate of barytes; as it parts with its excess of acid at a moderate heat, which by no means is the case with supersulphate of potash.

& Jour. de Phys. xlv. 13.

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This man found a Bologna stone at the foot of Mount Chap. III. Paterno, and its brightness and gravity made him suppose that it contained silver. Having exposed it to the fire, doubtless in order to extract from it the precious metal, he observed that it was luminous in the dark. Struck with the discovery, he repeated the experiment, and it constantly succeeded with him. It is evident that by the calcination it must be converted, at least partly, into sulphuret.

The following Table exhibits the result of the different experiments hitherto made to ascertain the composition of this salt.

	†	1	ş	11	¶	**	++
Acid	24	25.18	31	32	33	33.96	34
Base	76	74.82	69	68	67	66.04	66
Total	100	100	100	100	100	100	100

These results differ very considerably from each other. The analysis of Kirwan seems most correct. It is of great importance to have an exact analysis of this salt, as it is by means of it that the proportion of sulphuric acid in different compounds is determined.

+ Chenevix, Nicholson's Jour. ii. 196. † Thenard, Ann. de Chim. xxxii. 266. || Vauquelin, Ann. de Chim. 1. 168.

Kirwan and Klaproth, Gehlen, v. 515.

\*\* Aiken, Nicholson's Jour. xxii. 304.

§ Bucholz, Beitrage, iii. 31.

++ Fourcroy, ili. 25-

Composition.

# Sp. 17. Sulphate of Strontian.

THIS salt, for the discovery of which we are indebted to Dr Hope and Mr Klaproth, may be composed artificially by dropping sulphuric acid into strontian water; in which case it has the form of a white powder. But it exists abundantly in different parts of the world, usually crystallized in rhomboidal prisms.

Properties.

This salt is tasteless. It is soluble in 3840 parts of boiling water. Sulphuric acid dissolves it readily when assisted by heat, but it is precipitated by the addition of water to the solution \*. In the greater number of its properties it has a considerable resemblance to sulphate of barytes.

Composition.

54 strontian

#### 100

58 strontian

#### 100

This salt is soluble in sulphuric acid, and therefore forms an imperfect supersulphate \*\*.

Hope, Trans. Edin. iv. 10.
 Beitrage, ii. 97.
 Ibid p. 137.
 Hume, Pbil. Mag. xiv. 358.

† Jour. de Min. An. vi. 6. § Nicholson's Journal, iii. 39. †† Ibid. p. 215.

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Division III.

## SULPHATES,

Chap. IIL

685

SUCH are the properties of the sulphates. The following Table exhibits the solubility of each salt in water, and the proportion of the constituents, as far as ascertained. They are all insoluble in alcohol :

Sulphates of	Solubility in 100	Constituents.				
ourprises or	Water.	Acid.	Base.	Water.		
Ammonia	50	100	26.05	57		
Magnesia	100	100	57.92	182.8		
Lime	0.55	100	76.70	55*8		
Soda	35	100	78-32	246.6		
Potash	6.2	100	130	20		
Strontian	0.0	100	138			
Barytes	0.0	100	203	1803		

THE SOL-

THE genus sulphates contains several salts of considerable importance.

1. Sulphate of potash was formerly used in medicine; but on account of its disagreeable taste and little solubility it is now laid aside. Apothecaries, indeed, sometimes use it to facilitate the powdering of vegetable eathartics. To the alum-makers it is of considerable importance, as it enters into the composition of alum, which cannot be obtained crystallized without potash ar ammonia.

Book II. Division III. 2. Sulphate of soda is one of the most common of all the *cooling purgatives*, as they have been termed; immense quantities being annually manufactured and consumed.

3. Sulphate of ammonia is sometimes employed in chemical analyses. Thus it was used with advantage by Hatchett in examining the molybdate of lead.

4. As great quantities of the sulphate of magnesia are prepared for commercial purposes, the salt is probably in common use on the continent as a purgative. Its intensely bitter taste has brought it into disuse in this country. What is sold by apothecaries under the name of Epsom salt is often nothing else than sulphate of soda in small irregular crystals.

5. Sulphate of lime is much used as a cement, under the name of *plaster of Paris*. It is employed also for moulds, and for casting into statues, &cc. It is first heated, in order to deprive it of its water. In this state it forms with water a liquid paste, which in a few minutes becomes solid in consequence of the combination of the water with the sulphate. It constitutes the chief ingredient of stucco; and is in many places used as a manure.

6. The sulphates of barytes and strontian are not applied to any useful purpose directly; but they furnish almost all the barytes and strontian which the chemists employ.

7. But the most important of all the sulphates is undoubtedly alum, which is applied by manufacturers to too many uses for a complete enumeration. To the dyer and calico printer this salt is indispensible; as alumina, its earthy base, forms one of the best of all the mordants, or substances which have the property of fix-

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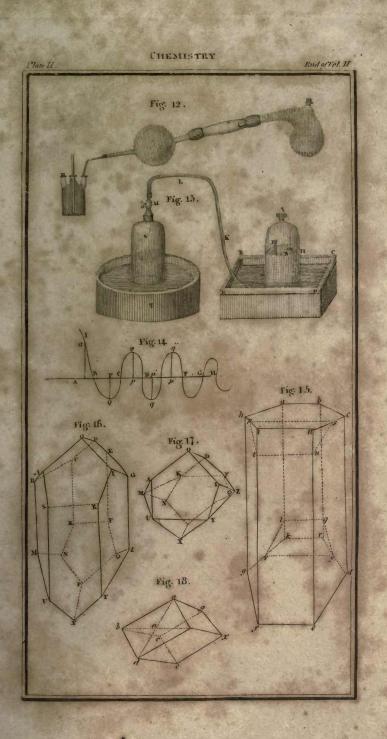
ing colouring matters in cloth. It is used by the tanners in the preparation of leather. Indeed, some kinds of leather may be considered as nothing else than skins altered by being steeped in a solution of alum in water. It is often very useful in clarifying liquors, from the property which alumina has of forming an insoluble precipitate with many vegetable substances. Surgeons sometimes take advantage of the properties of this salt, and use it as an astringent or styptic; but it would be too tedious to enumerate the purposes to which this salt is applied by paper-makers, goldsmiths, candle-makers, bookbinders, &c.

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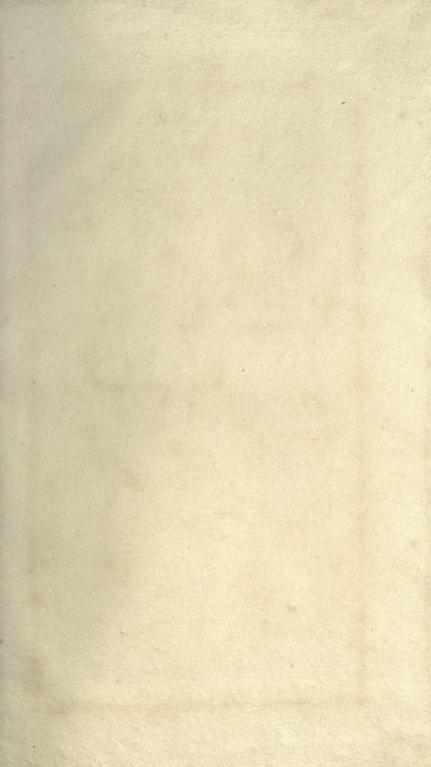
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